VOL. XX. FEBRUARY, 1898. NO. 2.

AMERICAN CHEMICAL JOURNAL

ON THE ACTION OF ACETIC ANHYDRIDE ON PHENYLPROPIOLIC ACID.

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Several years ago,[1] we showed that acetic anhydride reacts with acetylenedicarboxylic acid to form the anhydride of acetoxylmaleïc acid, and that this compound gives oxalacetic acid on treatment with water. If acetic anhydride should react with phenylpropiolic acid in an analogous manner, the anhydride of β-acetoxylcinnamic acid would be formed, and this compound on decomposing with water would yield a β-hydroxycinnamic acid. It seemed of theoretical interest to ascertain whether a product obtained in such a manner is identical with the benzoylacetic acid[2] gotten by saponification of its ester, but this object was not realized, as it was apparent from the preliminary experiments that acetic anhydride reacts on phenylpropiolic acid, in an entirely different manner than on acetylenedicarboxylic acid.

The new product has the composition of phenylpropiolic anhydride, but its properties showed that such a constitution is impossible. On treating it with alkalies it goes into solution, and addition of a mineral acid gives a precipitate of the original anhydride, not of phenylpropiolic acid, which

[1] Ber. d. chem. Ges., **28**, 2511. [2] Perkin: J. Chem. Soc., **43**, 174.

should be formed if it were the anhydride of this acid. This behavior shows also that at least two molecules of phenylpropiolic acid enter into the reaction, and also that the substance cannot be the anhydride of symmetrical triphenylmesic acid. The reduction of the substance in alkaline solution yields an acid that no longer spontaneously gives an anhydride, and with the composition of the truxillic acids; but not identical with any known acid of that series. By an investigation of the original anhydride we have been able to classify it as a derivative of naphthalene, and we reserve the discussion of this peculiar reaction until we describe our experimental results.

Preparation of the Anhydride, $C_{18}H_{10}O_3$.

The phenylpropiolic acid used in our work was usually made by the action of alcoholic potash on $\alpha\beta$-dibromhydrocinnamic ester, as we found that the impure acid obtained in this way gave the new product in a pure condition. In our earlier experiments the acid and anhydride were heated in sealed tubes to 100°, but later we found that the reaction takes place easily on boiling these substances in a flask connected with a return cooler. The method of procedure can be best illustrated by describing two of the actual experiments in detail.

28.5 grams of phenylpropiolic acid and 57.9 grams of acetic anhydride were heated in a sealed tube at 100° for seven hours. The acid went into solution at once, and after warming for some time a substance began to separate in large, transparent, tabular crystals. The cold tube showed no pressure on opening, and the crystals, after washing with a little acetic acid and drying, weighed 13.6 grams. The mother-liquor was distilled off *in vacuo* at 100°, and the oil thus obtained became solid on standing in the cold. On treating with a small quantity of cold absolute ether all the substance, except 0.39 gram, went into solution, and the insoluble substance proved to be the same product as the 13.6 grams. The ether was driven off from the filtrate *in vacuo*. On standing the thick oil solidified, and was purified by washing with dry benzene, then crystallizing from a hot carbon tetrachloride and benzene. It forms crystals hav-

ing a cubical appearance, and melting at 72°–74°. An analysis of the substance, dried *in vacuo*, gave the following figures:

0.18379 gram substance gave 0.3325 gram CO_2, and 0.0480 gram H_2O.

	Theory for $(C_6H_5—CH—CBr—CO)_2O$.	Found.
C	49.52	49.36
H	2.93	2.90

The results show that the compound has the composition of the anhydride of bromcinnamic acid, and to ascertain to which of the acids it corresponds, it was dissolved in cold alkali, and the precipitate formed by addition of hydrochloric acid crystallized from hot water. The acid so obtained melted at 120°, and possessed the other properties of allo-α-bromcinnamic acid. Its identity was further confirmed by an analysis.

	Theory for $C_6H_5—CH—CBr—COOH$.	Found.
C	47.58	47.88
H	3.07	2.98

The formation of this anhydride is evidently due to the presence of allo-α-bromcinnamic acid in the phenylpropiolic acid. In decomposing $\alpha\beta$-dibromhydrocinnamic ester with caustic potash a mixture of α- and allo-α-bromcinnamic acids are formed, and of these two acids only the higher-melting isomer is readily further split into phenylpropiolic and hydrobromic acids. For this reason the method described by Perkin[1] for the preparation of phenylpropiolic acid always gives a mixture of this acid and allo-α-bromcinnamic acid; in fact, some of our preparations contained as much as 30–40 per cent. of the brom-acid. This mixture, however, may be satisfactorily used in the reaction, as it is easy to separate the two products, and the allo-α-bromcinnamic anhydride may be converted by esterization with hydrochloric acid into α-bromcinnamic ester, from which product phenylpropiolic acid may be obtained in almost theoretical amount. To prepare the substance in an open flask, connected with a return-condenser, 100 grams each of impure phenylpropiolic acid and acetic anhydride were heated until the liquid began to boil, when the burner was

[1] J. Chem. Soc., **45**, 142.

removed. The reaction once begun evolved considerable heat, so that the solution kept boiling about five minutes; on cooling, crystals began to separate, when the boiling recommenced, and then continued for some minutes longer. On standing, 45 grams of pure substance were deposited, and by boiling the mother-liquor for several hours, a further deposit of 6 grams was obtained. In our subsequent preparations we boiled the solution for one-half hour after the heat of the reaction had moderated, and found this heating sufficient to complete the decomposition. The yield was about 50–60 per cent. of the phenylpropiolic acid taken, but if a pure acid were used it would probably not be far from the theoretical. After washing the crystals with acetic acid, they were powdered, and crystallized from boiling cumene.

I. 0.1657 gram of substance, dried *in vacuo* at 100°, gave 0.4793 gram of CO_2 and 0.0547 gram of H_2O.

II. 0.1503 gram of substance, dried *in vacuo* at 100°, gave 0.4362 gram of CO_2 and 0.0490 gram of H_2O.

	Theory for $C_{18}H_{16}O_3$.	Found. I.	II.
C	78.83	78.89	79.15
H	3.65	3.67	3.62

The crystals obtained in the preparation of the substance are transparent, hard, rectangular prisms, many of them with truncated angles, and melting at 255°, although it begins to soften at 230°. In this state the substance is very resistant to the action of ordinary solvents, even to alkaline solutions, but may be recrystallized from boiling acetic anhydride or cumene. If the substance is brought into solution by boiling with alkalies, and the solution acidified, it comes down as a pasty mass, which soon solidifies, and in this condition it is easily soluble in alcohol, glacial acetic acid, acetic ester, acetone and sodium carbonate. The difference in solubility is due, however, to a different state of aggregation, and not to a chemical change. Heated in an open tube, it boils and condenses on the sides of the tube, without essential decomposition.

The molecular weight was determined according to Eykman's method, and the following results obtained:

	Phenol. Grams.	Substance. Grams.	Δ.	Molecular weight.
I	12.9062	0.1770	0°.39	267
II	12.8100	0.2694	0°.62	258
III	12.7972	0.3534	0°.81	259

Mean = 261

Calculated for $C_{18}H_{10}O_3$ = 274

Salts of the Acid, $C_{18}H_{12}O_4$.

It has been already noticed that the substance can be dissolved in alkalies, when it goes over into a salt of an acid, and on addition of a mineral acid to this solution the original anhydride is precipitated. This relationship is similar to that shown by certain unsaturated, dibasic acids like the dialkylmaleïc acids; and the above property seemed to indicate that the unstable carboxyls are in a side chain, as the property of forming an anhydride spontaneously has not been observed with carboxyls existing in the benzene nucleus.

The sodium salt was prepared by boiling the anhydride in a flask with a return-condenser, with the theoretical amount of pure sodium hydrate, dissolved in ten parts of water, until complete solution, and filtering the thick mass of crystals under pressure, which were deposited as the solution cooled. These crystals were washed once with a little water, then thoroughly with 50 per cent. alcohol. A further quantity may be obtained by adding an excess of caustic soda to the filtrate, as it is much less soluble in an excess of alkali than in water. The salt forms white, glittering, prismatic plates, that are obliquely truncated, and in aqueous solution it does not show the permanganate test for unsaturated acids.

I. 0.6262 gram air-dried salt, dried first at 100°, then 130°, and finally at 165°–170°, under 20 mm., lost 0.1197 gram H_2O.

II. 0.5872 gram air-dried salt gave 0.1994 gram Na_2SO_4.

III. 2.3640 grams air-dried salt gave 0.8108 gram Na_2SO_4.

	Theory for $C_{18}H_{10}O_4Na_2.4\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	19.65	19.11	....	....
Na	11.04	....	11.12	11.12

The barium salt was made by adding barium chloride to a solution of the sodium salt, and was deposited as a granular pre-

cipitate, which seen under the microscope consisted of obliquely-truncated prisms.

I. 0.4544 gram of air-dried salt, heated gradually to 165°, lost 0.0558 gram H_2O.

II. 0.4290 gram of air-dried salt gave 0.2002 gram $BaSO_4$.

	Theory for $C_{18}H_{10}O_4Ba.3H_2O$.	Theory for $C_{18}H_{10}O_4Ba.4H_2O$.	Found. I.	Found. II.
H_2O	11.23	14.43	12.27	....
Ba	28.50	27.46	....	27.44

The water of crystallization is evidently expelled with difficulty, which accounts for the low results in the direct determination.

In a similar manner the calcium salt was obtained as a crystalline precipitate.

0.7175 gram salt, air-dried, lost 0.0846 gram H_2O at 200°.

0.7175 gram salt, air-dried, gave 0.2551 gram $CaSO_4$.

	Theory for $C_{18}H_{10}O_4Ca.3H_2O$.	Found. I.	Found. II.
H_2O	14.06	11.79	....
Ca	10.42	....	10.45

The salt evidently contains three molecules of water of crystallization, all of which is not expelled at 200°.

Solutions of silver nitrate and the sodium salt give a white, granular precipitate of the silver derivative, which changes but slowly on exposure to light.

0.2319 gram of air-dried salt gave 0.0956 gram Ag.

0.2846 gram of air-dried salt lost 0.0018 gram H_2O when heated to 100° for 45 minutes, and 0.1203 gram Ag.

	Theory for $C_{18}H_{10}O_4Ag_2$.	Found. I.	Found. II.
Ag	42.59	41.22	42.59

All of the above salts give the original anhydride on decomposition with acids, and it is evident from these results that the dibasic acid, $C_{18}H_{12}O_4$, cannot exist in a free state, but decomposes on liberation from its salts into the anhydride, $C_{18}H_{10}O_3$, and water.

To obtain the methyl ester the anhydride with four parts by weight of methyl alcohol and one-half part of sulphuric acid was boiled for four hours. On standing in a cool place

crystals were deposited, which, after treatment with sodium carbonate solution, consisted of the ester. The mother-liquor, poured into water gave a pasty mass, which gradually solidified on being rubbed with a pestle, under a solution of sodium carbonate. The yield of ester obtained in this way is far from satisfactory, being only about one-third the weight of the anhydride used in the experiment. A better result was gotten by treating the air-dried silver salt in a sealed tube with methyl iodide. The reaction proceeded in the cold, and was complete after heating one hour at 100°. The precipitate, consisting of silver iodide and methyl ester, was extracted with hot alcohol, and the crystals deposited on cooling treated with a cold solution of sodium carbonate. The insoluble residue was purified by several crystallizations from alcohol, and gave the following analytical results:

0.2549 gram ester gave 0.6964 gram CO_2 and 0.1153 gram H_2O.

0.2395 gram ester gave 0.6572 gram CO_2 and 0.1092 gram H_2O.

	Calculated for $C_{14}H_{10}(COOCH_3)_2$.	Found. I.	II.
C	75.00	74.63	74.84
H	5.00	5.05	5.07

The ester crystallizes from alcohol in white prisms, that melt at 118°–120°. It dissolves readily in hot methyl alcohol and ethyl alcohol, and carbon tetrachloride, less readily in hot ether; in these solvents, when cold, it is moderately soluble. Saponified with alkalies the solution gave a precipitate of anhydride on acidifying. A solution of ester in carbon tetrachloride was slowly acted on by bromine on exposure to light, but an addition-product was not formed.

Molecular weight determinations[1] of the ester, according to Eykman's method, gave the following results:

[1] We are indebted to Dr. V. L. Leighton for these determinations, as well as for those of the anhydride.

	Phenol. Grams.	Substance. Gram.	Δ.	Molecular weight.
I	11.8128	0.1422	0°.2575	355
II	11.7200	0.6652	1°.3625	317
III	11.6900	0.8440	1°.6975	323

Mean = 332
Theory = 320

Primary Product of the Action of Acetic Anhydride on Phenylpropiolic Acid.—In one of our experiments we heated pure phenylpropiolic acid with four times its weight of acetic anhydride in a sealed tube for a short time at 100°. The acid went into solution, but no anhydride was deposited on cooling. The product was distilled *in vacuo*, and remained liquid until almost all the acetic anhydride was expelled, when, as the water-bath was heated to almost 100°, the residue solidified, and now consisted of the anhydride and a small amount of oil. Evidently the anhydride must have been formed during the process of heating on the water-bath, as otherwise it would have been deposited as the contents of the tube were cooled. We were led by this result to endeavor to isolate the product first formed in this reaction.

A quantity of pure phenylpropiolic acid was placed in a sealed tube with five times its weight of acetic anhydride, and, after standing five days at ordinary temperature, the product was evaporated, *in vacuo*, over caustic soda, when the greater part of the phenylpropiolic acid was recovered unchanged.

A second quantity of phenylpropiolic acid was dissolved in four parts of acetic anhydride, allowed to stand for twelve hours, then evaporated at ordinary temperature *in vacuo*, and this operation repeated twice. After the last treatment it was allowed to stand in a partial vacuum for a week, and then consisted of an oil and a small quantity of a solid, which was found to be a mixture of the anhydride and phenylpropiolic acid. On further standing more of these substances slowly separated from the oil, and, as it was apparently decomposing with the formation of the anhydride, the oil was decanted and analyzed.

0.1587 gram oil gave 0.4087 gram CO_2, and 0.0654 gram H_2O.

	Theory for $C_{11}H_8O_2$.	Found.
C	70.27	70.24
H	4.27	4.59

The oil dissolved very slowly in a solution of sodium carbonate, quickly in caustic alkalies, and acids precipitated phenylpropiolic acid from these solutions. In the filtrates the presence of acetic acid was proven. The substance $C_{11}H_8O_2$ is evidently the mixed anhydride of acetic and phenylpropiolic acids, with the constitution $C_6H_5—C—C—CO—O—OC—CH_3$.

Action of Aniline on the Anhydride, $C_{18}H_{10}O_3$.

The anhydride and aniline, in proportion of one to four equivalents, and some water were heated to 100°. The anhydride went into solution, and after a time a solid substance was deposited, which was purified by crystallization from alcohol.

0.1375 gram substance gave 0.3947 gram CO_2, and 0.0612 gram H_2O.

	Theory for $C_{18}H_{10}O_2.NH_2C_6H_5$.	Found.
C	78.47	78.79
H	4.63	4.95

The substance forms transparent crystals, that melt at 194° with decomposition. It is insoluble in water, and moderately in cold alcohol. Aqueous caustic soda does not effect solution, but converts it into a sticky mass. This property of the substance is not in accordance with the view that it is the acid anilide of the acid $C_{10}H_{10}(COOH)_2$. The substance was not further examined.

Action of Sodium Amalgam on the Sodium Salt, $C_{10}H_{10}(COONa)_2$.

A simple conception of the formation of the anhydride, $C_{10}H_{10}\begin{matrix}CO\\CO\end{matrix}O$ from phenylpropiolic acid is the polymeriza-

tion of two molecules to form a four-ring derivative. Such a tetramethine derivative should pass over on reduction to a tetramethylene product, which might be identical with one of the truxillic acids of Liebermann.[1] Contrary to this constitution is the comparative stability of the sodium salt towards potassium permanganate, but this indifference might possibly be due to the ring-constitution of the substance, as the permanganate test is characteristic only for fatty $\alpha\beta$-unsaturated acids. Twenty grams of the anhydride were dissolved in 8 grams of sodium hydrate, the solution diluted to 800 cc., and 800 grams of a four per cent. sodium amalgam gradually added. It is necessary to use a large excess of sodium amalgam, as otherwise the reduction-product will contain a considerable proportion of unreduced acid. The sodium salt of the reduced product is rather insoluble in strong alkali, so that the salt separated as prismatic crystals near the amalgam, but it gradually rose, and dissolved in the less concentrated layer of the liquid. The solution was partially neutralized, filtered, and acidified with sulphuric acid, when an oily substance was deposited, which gradually turned solid. This product is soluble in acetone, and is precipitated on concentrating the solution, or by adding benzene to it, but this method of treatment is not satisfactory, owing to the tendency of the substance to form a syrup. It is preferable to treat with hot acetic acid in sufficient quantity to dissolve almost the entire product, pour off from the undissolved substance, and recrystallize the precipitate formed on cooling, from the same solvent, until its melting-point becomes constant. The mother-liquors gave some more of the product, but the last part was always more or less gummy. It was analyzed with the following result:

I. 0.1660 gram substance, dried at 100°, gave 0.4440 gram CO_2, and 0.0806 gram H_2O.

II. 0.1936 gram substance, dried at 100°, gave 0.5149 gram CO_2, and 0.0986 gram H_2O.

	Theory for $C_{18}H_{16}O_4$.	Found. I.	II.
C	72.97	72.93	72.54
H	5.40	5.39	5.55

[1] Ber. d. chem. Ges., **21**, 2342: **22**, 124 and 2240.

The new acid forms white crystals that melt, under decomposition, at 200°–202°, but the melting-point depends on the rapidity of heating, and it melts with slow heating at 195°–198°. It is easily soluble in acetone and acetic ether, difficultly in cold water, and insoluble in carbon tetrachloride and benzene.

Neutralized with aqueous ammonia, its solution gave white crystalline precipitates with solutions of barium, calcium, and mercuric chlorides. Silver nitrate precipitates a white salt, that becomes crystalline on warming. It was dried *in vacuo*, then for thirty minutes *in vacuo* at 100°, and analyzed.

0.6824 gram salt gave 0.2933 gram Ag.

	Theory for $C_{18}H_{14}O_4Ag_2$.	Found.
Ag	42.83	42.35

A further reduction by sodium amalgam does not take place; as we boiled a solution of the sodium salt with a large excess of amalgam, and recovered only the unchanged acid, $C_{18}H_{16}O_4$. We also found that the acid, when heated with concentrated hydriodic acid and amorphous phosphorus, undergoes no change.

Anhydride of the Acid, $C_{18}H_{16}O_4$.

Three grams of acid and six grams of acetic anhydride were heated to 170° in a sealed tube. On cooling, the tube opened without pressure, and contained a clear solution that partially solidified on rubbing with a glass rod. The crystals were washed with acetic anhydride, and then recrystallized from this solvent. For analysis it was dried *in vacuo* at 100°.

0.1529 gram substance gave 0.4340 gram CO_2, and 0.0736 gram H_2O.

	Theory for $C_{18}H_{14}O_3$.	Found.
C	77.15	77.41
H	5.06	5.33

The anhydride is a white crystalline solid, that melts at 145°–150°. It dissolves on warming with caustic soda, and mineral acids precipitate the original acid from this solution. The acid $C_{18}H_{16}O_4$ is not only iso-

meric with the truxillic acids, but resembles the β-acid of this group in its properties. It is not identical with it, however, as β-truxillic anhydride[1] has different properties from the compound just described, a conclusion which is confirmed by the behavior of our acid towards aniline. Equal weights of acid and base were boiled for fifteen minutes. On cooling, a sticky mass was obtained, which was treated with dilute hydrochloric acid and caustic soda, and then washed with dilute alcohol. The substance remained in a semi-solid condition, and could not be brought to crystallize, whereas the β-truxillanil forms a crystalline, high-melting compound.[2]

Behavior of the Acid, $C_{18}H_{16}O_4$, *on Oxidation with Potassium Permanganate.*

Two grams of the acid were dissolved in an excess of dilute caustic soda and 120 cc. of a 5 per cent. solution of permanganate, added in six portions, the solution being allowed to become colorless before each new addition. The first 60 cc. of the permanganate were reduced almost entirely, while the last 20 cc. were only nearly decolorized after twenty-four hours; a further addition of 5 cc. made the solution retain the permanganate color, even after standing two days. After each decolorization the manganese dioxide was filtered, washed with water, and examined for organic matter, but only the first precipitate contained a trace, which was insoluble in sodium carbonate, and did not give the alcoholic potash test for benzil. On evaporating the filtrates and acidifying, a yellowish, viscous product separated, which could not be brought into a crystalline state, nor purified, and was therefore not further examined. This experiment further established the fact that our product is not identical with β-truxillic acid, as that substance gives benzil when treated as above.[3]

Reduction of the Anhydride, $C_{18}H_{16}O_3$, *in Acetic Acid Solution.*

Five grams of anhydride were dissolved in 50 cc. of acetic

[1] Liebermann and Sachse: Ber. d. chem. Ges., **26**, 835.

[2] Liebermann and Sachse, *loc. cit.*, used anhydride in their experiment, but there can be but little doubt that the acid would give the same result. We obtained a neutral substance, like an anil, which certainly showed entirely different chemical and physical properties from their product.

[3] Liebermann: Ber. d. chem. Ges., **22**, 2254.

acid and 20 grams water, and 15 grams zinc dust added. After boiling for four hours in a flask with return-cooler, 10 cc. water were added, and the mixture again heated for three hours. On pouring into dilute sulphuric acid, an organic substance was deposited, which melted from 130°–190°. The crude product was rubbed for several minutes with a 5 per cent. solution of sodium carbonate, filtered, and the residue again treated in the same way, when all the acid was removed. The insoluble residue was purified by several crystallizations from alcohol and analyzed.

0.1519 gram substance, dried at 100°, gave 0.4614 gram CO_2, and 0.1519 gram H_2O.

	Theory for $C_{18}H_{12}O_3$.	Found.
C	83.08	82.84
H	4.62	4.63

The white crystalline substance melted at 135°–137° without decomposition. Its behavior towards sodium carbonate shows that it is a neutral body, and it follows from this property and its composition, that it must be a lactone, formed by replacing an oxygen of carbonyl by two hydrogen atoms.

Oxidation of the Anhydride, $C_{18}H_{10}O_3$, *with Potassium Permanganate.*

A large number of oxidation experiments, in which the conditions were variously modified, were made in the hope that the results would throw some light on the constitution of the anhydride. The sodium salt of the acid, $C_{18}H_{14}O_4$, is considerably more easily oxidized by permanganate than that of the acid, $C_{18}H_{12}O_4$; in fact the first product behaves towards this reagent like an unsaturated fatty acid, whereas the second could not be so classified. To judge from this property, the unsaturated part of the acid, $C_{18}H_{12}O_4$, cannot belong to an unsaturated fatty side chain, and the relation of the reduced to the original body, in its susceptibility to oxidation, agrees with the assumption that the reduction has gone on in the aromatic nucleus of the compound.

Ten grams of the anhydride, $C_{18}H_{10}O_3$, were dissolved

in an excess of caustic soda, the solution diluted and made neutral by addition of sulphuric acid. To this solution a 5 per cent. solution of potassium permanganate, in portions of 10 cc., were added, waiting for decolorization before adding a fresh portion. The first portions of the oxidizing agent were reduced in ten to twenty minutes, but towards the end the oxidation proceeded very slowly. In all, 54 grams of potassium permanganate were used until no, or only extremely slow, oxidation occurred. The solution was decolorized by addition of sodium sulphite, filtered, concentrated on the water-bath, acidified with sulphuric acid, and extracted with ether. On removing the ether, a very viscous oil remained, which, placed in a vacuum, formed a large bubble, expanding until the upper part of the bell-jar was almost completely filled. On long standing in a vacuum the product became friable, and could be pulverized, and then weighed 14 grams. This product was dissolved in dry acetone, and the precipitate, formed by slow evaporation, dried and analyzed (I).

In a second experiment 17 grams of anhydride were dissolved in caustic soda, the solution diluted to 1500 cc., and 90 grams of powdered potassium permanganate added. The solution was warmed on a water-bath, shaken until all the permanganate had gone into solution, and then heated four hours to boiling in a flask with a return-cooler. On cooling, the solution was decolorized with sodium sulphite, and worked up as described in the preceding experiment. 22 grams of crude product were obtained. This was dissolved in dry acetone and some benzene added, when part of the substance came down in crystalline form. The mother-liquor gave a syrup which, as it could not be brought to crystallize, was dissolved in alkali, acidified and extracted with ether. A friable product was obtained, which was boiled with glacial acetic acid, to remove a sticky substance, dissolved in dry acetic ester and some glacial acetic acid added to the solution. On warming gently the acetic ester was gradually expelled, and a crystalline substance separated. It was filtered, washed with a mixture of acetic ester and acid, and, after drying *in vacuo* at 100°, it was analyzed (II).

As the above product did not show a sharp melting-point, it began to turn yellow at 230°, and was not completely melted until 280°; the rest of it was dissolved in hot acetic ester and recrystallized after addition of acetic acid. There was no change in the melting-point, and an analysis (III) showed that the substance was in a pure state.

I. 0.1263 gram substance gave 0.2687 gram CO_2, and 0.0395 gram H_2O.

II. 0.1608 gram substance gave 0.3424 gram CO_2, and 0.0500 gram H_2O.

III. 0.1626 gram substance gave 0.3455 gram CO_2, and 0.0495 gram H_2O.

	Theory for $C_{16}H_{10}O_8$.	Theory for $C_{18}H_{12}O_9$.	Found. I.	II.	III.
C	58.18	58.01	58.02	58.07	57.95
H	3.33	3.23	3.47	3.45	3.38

The white, crystalline acid is slowly soluble in cold, quickly in hot, water. Obtained by evaporation of its solution in ether, it is difficult to get it back into solution by the same solvent, but it dissolves readily in acetic ester and alcohol, and is almost insoluble in benzene, acetic acid, acetone, chloroform and carbon tetrachloride. After crystallization from a mixture of acetic ester and acid, it only dissolves in acetic ester and acetone after protracted boiling. The acid may be heated to 150°–160° with concentrated hydriodic acid and phosphorus without undergoing change.

Silver Salt.—This derivative was made by adding aqueous silver nitrate to a neutral solution of the acid in ammonia, and forms a white precipitate.

I. 0.6467 gram salt, dried to constant weight *in vacuo*, gave 0.3637 gram Ag.

II. 0.5023 gram vacuum-dried salt did not lose weight by drying for one-half hour at 100°, and gave 0.2823 gram Ag.

III. 0.5750 gram salt, dried for a short time *in vacuo*, gave 0.3262 gram Ag.

	Theory for $C_{12}H_8(COOAg)_4$.	Theory for $C_{14}H_8(COOAg)_4$.	Found. I.	II.	III.
Ag	56.99	55.10	56.24	56.20	56.73

Barium Salt.—Obtained from the ammonium salt as a white crystalline precipitate by addition of barium chloride. This

salt often requires considerable time before separating, but heating the solution brings it down at once. The following experiments afford an approximate determination of its solubility; 0.2 gram neutralized acid in 160 cc. water (1 acid to 800 water) gave no precipitate in the cold, but one was formed on heating, that did not redissolve on standing in the cold. In another test, with double the quantity of water, no salt was formed, even after heating the solution.

I. 0.4577 gram air-dried salt, lost 15.6 per cent. water at 190°,[1] and gave 0.2885 gram $BaSO_4$.

II. 0.4000 gram air-dried salt lost 15.45 per cent. water at 200°, and gave 0.2525 gram $BaSO_4$.

III. 0.2512 gram air-dried salt gave 0.1591 $BaSO_4$.

	Theory for $C_{16}H_8O_8Ba_3.8H_2O$	Found. I.	II.	III.
Ba	36.86	37.07	37.24	37.12

The *calcium salt* is soluble in water; and a *lead salt* is deposited as an insoluble, white substance by addition of lead acetate to a solution of the acid.

The results obtained with the silver salt indicate that the acid is tetrabasic, and this view as was confirmed by titration of the acid with caustic potash. 0.1017 gram crystallized oxalic acid required 5.96 cc. of the alkaline solution in use

0.1019 gram of the acid required 4.45 cc. potassium hydrate solution. Calculating from these results the molecular weight of the tetrabasic acid would be 337.5, while the molecular weight of $C_{16}H_{10}O_8$ is 330. As the molecular weight of the acid deduced from the analyses of the silver salts is 333.5, it is very probable that the acid is tetrabasic, providing its molecular weight is not a multiple of the above number.

Methyl Ester.—We prepared this compound in the hope of obtaining a derivative of the acid with a sharp melting-point, and to establish its molecular weight with greater certainty. The vacuum-dried silver salt, and an excess of methyl iodide, and some dry ether, were sealed in a tube, and warmed gently at first, finally heated to 100° for an hour. On standing over night, large crystals had separated from the supernatant liquid. Absolute alcohol was added to the mixture and, after heating

[1] The water of crystallization cannot be completely expelled without decomposition of the acid.

for some time, it was filtered hot. On cooling considerable substance separated, but a minute quantity of silver iodide was also deposited, which could not be perfectly separated from the ester by repeated crystallizations from alcohol. The greater part of the alcohol was driven off, the precipitate dissolved in boiling chloroform, and the solution filtered from the insoluble silver iodide. The product was obtained pure by recrystallizing three times from carbon tetrachloride.

I. 0.1503 gram ester, dried at 100°, gave 0.3421 gram CO_2, and 0.0650 gram H_2O.

II. 0.1946 gram ester, dried at 100°, gave 0.4398 gram CO_2, and 0.0838 gram H_2O.

III. 0.2160 gram ester, dried at 100°, gave 0.4902 gram CO_2, and 0.0912 gram H_2O.

IV. 0.2025 gram ester, dried at 100°, gave 0.4606 gram CO_2, and 0.0940 gram H_2O.

	Theory for $C_{12}H_4(COOCH_3)_4$.	Theory for $C_{14}H_2O(COOCH_3)_4$.	Found. I.	II.	III.	IV.
C	62.18	61.68	61.91	61.66	61.91	62.03
H	4.66	4.67	4.69	4.79	4.69	5.19

The ester crystallizes in large, transparent rhombohedrons, that melt at 130°–133°. It is soluble in hot alcohol, methyl alcohol, chloroform and carbon tetrachloride; only moderately in these solvents when cold. The molecular weight of the ester was determined by the freezing-point method, glacial acetic acid being used as the solvent.

	Acetic acid. grams.	Substance. gram.	Δ	Molecular weight.
I	20	0.5056	0°.28	351
II	20	0.0740	0°.47	400

Mean = 376
Theory for $C_{12}H_4(COOCH_3)_4$ = 386
Theory for $C_{14}H_2O(COOCH_3)_4$ = 428

The difference between the carbon percentages in the above formulae is only 0.5 and that of hydrogen is practically the same, and although the analytical results indicate that the acid contains sixteen atoms of carbon, it is impossible to decide with certainty between the two possible formulae. The evidence from the molecular weight determinations is also in

favor of the simpler composition, but here too the figures are too close for a sure proof. These last results prove, however, that the acid is tetrabasic, as was made probable from the study of its metal salts.

Benzyl Ester.—A little less than the theoretical amount of benzyl iodide, dissolved in dry ether, was added gradually to the dry silver salt, and the tube containing it kept cool during the operation. It was then sealed, and heated for 12 hours at 100°. The silver iodide was filtered, and the oily filtrate shaken with dilute, aqueous sodium carbonate. On standing three layers were formed, the middle one consisting of the alkaline solution. The upper layer was warmed until the ether was driven off, and a crystalline substance left, which was crystallized from glacial acetic acid.

0.1586 gram ester gave 0.4445 gram CO_2, and 0.075 gram H_2O.

	Theory for $C_{12}H_6(COOCH_2C_6H_5)_4$.	Theory for $C_{14}H_8O(COOCH_2C_6H_5)_4$.	Found.
C	76.52	70.59	76.26
H	4.93	4.31	5.25

The ester forms a white crystalline substance, that melts at 114–118°. Heated with alkalies, in a sealed tube at 100°, the ester is saponified, and the original acid was regained from the product of the reaction.

The large difference between the carbon-percentages in the above formulae, almost 6 per cent., and the analytical results obtained in the combustion of the ester, leave no doubt that the orginal acid has the composition, $C_{12}H_6(COOH)_4$.

Anhydride of the Acid, $C_{12}H_6(COOH)_4$.

A portion of the acid was heated with twice its weight of acetic anhydride to 150°–170° for three hours, and the product of reaction evaporated to dryness *in vacuo*. The residue was washed with a little benzene, and then crystallized from boiling xylene.

0.1373 gram substance, dried at 100°, gave 0.3263 gram CO_2, and 0.0310 gram H_2O.

	Theory for $C_{12}H_6[(CO)_2O]_2$.	Found.
C	65.31	64.91
H	2.04	2.51

The anhydride is a light-yellow crystalline body. Treated with alkalies it goes into solution, forming a salt of $C_{12}H_6(COOH)_4$.

Hydrocarbon from the Acid, $C_{12}H_6(COOH)_4$.

An intimate mixture of barium salt of the acid with about twice its weight of dry barium hydrate was rapidly heated in a glass tube, a current of hydrogen being passed over it at the same time. The distillate was extracted with dilute sodium hydrate, then with ether, and the solid residue remaining after evaporation of the solvent, crystallized several times from alcohol. The hydrocarbon possessed the melting-point (71°) and the other properties of diphenyl, and its identity with that substance was further confirmed by analysis.

0.0757 gram substance gave 0.2590 gram CO_2, and 0.0467 gram H_2O.

	Theory for $C_{12}H_{10}$.	Found.
C	93.50	93.31
H	6.49	6.85

It is evident from the conversion of the acid $C_{12}H_6(COOH)_4$ into diphenyl that the acid is a tetracarboxyl derivative of this hydrocarbon, but it still remains to show the distribution of the carboxyl in the molecule. Further investigation of the acid was rendered unnecessary, as its full constitution conclusively follows from the constitution proven farther on for the original anhydride.

Second Acid Formed in the Oxidation of the Anhydride, $C_{14}H_{10}(CO)_2O$.

In all our oxidation experiments we invariably obtained a sticky mass in the acetic acid mother-liquors, which on standing in a vacuum gradually became friable, but could not be brought into a crystalline condition. The solubilities of this product left no doubt as to its difference from the oxidation-product already described, although there was no certainty of a perfect separation of the two products by the method used. The examinations of the salts of the two products showed that the separation could easily be effected by means of the barium salts, as this derivative of the amor-

phous acid is very soluble in water, while the crystalline acid, as is already shown, gives a very insoluble salt. The relative proportion of amorphous to crystalline product varies somewhat according to the manner of oxidation. Our experiments indicate that the best yield of the crystalline product was obtained in those cases, in which the oxidation was affected by adding a large quantity of potassium permanganate, allowing it to act for a long time at a low temperature, and finally heating the solution in a water-bath; but in no case did we obtain more than 50 per cent. of this product. On the other hand, adding the permanganate to the solution, and effecting the oxidation quickly, gave the best result for the amorphous product. A large number of oxidation experiments were made, but we describe here only one of them in order to show our method of procedure.

37 grams of the anhydride, $C_{15}H_{10}O_3$, were dissolved in caustic potash, the solution diluted to one liter, and then a solution of 86 grams of permanganate in 1500 cc. water were added in several portions. The temperature of the solution was 29° before the addition, but it gradually rose, and in about 45 minutes it reached its maximum of 50°. After standing an hour and a half, the solution was decolorized, and after further addition of 8 grams permanganate, the solution was heated on the water-bath, when it decolorized on heating several hours. The solution was filtered, the filtrate concentrated to 400 cc., then neutralized with hydrochloric acid, and an excess of a hot concentrated solution of barium chloride added. After standing some hours the precipitate was removed, and the filtrate acidified with hydrochloric acid and extracted with ether. The ether extract was shaken out with a titrated solution of caustic potash, it requiring 14.4 grams caustic potash, which corresponds to 23 grams of acid, assuming it to be a tetrabasic acid with the molecular weight 360. This solution, which did not give a precipitate with barium chloride even after concentration, was evaporated to 100 cc. and used for the following experiments: A portion was acidified, extracted with ether and portions of the viscous acid left on evaporation of the solvent boiled with the carbonates of magnesium, lithium, strontium, calcium and zinc,

but in all cases only soluble amorphous salts were obtained. Another portion of the solution was treated with aqueous silver nitrate, when an almost white, granular precipitate of the silver salt was deposited.

0.6777 gram salt, dried *in vacuo*, first at ordinary temperature, then for one-half hour at 60°, gave 0.3626 gram Ag.

	Theory for $C_{13}H_8(COOAg)$.	Found.
Ag	56.99	53.52

Although the result only approximately agrees with that required by theory, it indicates that the acid is tetrabasic, providing the molecule of the anhydride, $C_{18}H_{10}O_3$, was not split into two molecules in the oxidation.

36 grams of the vacuum-dried silver salt with 70 grams dry ether and 40 grams methyl iodide were mixed in a sealed tube with cooling, and, after the reaction ceased in the cold, the tube was heated for two hours to 100°. On working up the product of the reaction 7 grams of a neutral, and three grams of an acid, oil were obtained. The neutral oil became solid on standing in a vacuum, and was soluble in ether, benzene, chloroform, acetic ester and acid, but not in petroleum ether. It decomposed when an attempt was made to distil it in a vacuum. All attempts to obtain this product in crystalline form were fruitless, but by dissolving it in alcohol, adding some water, and placing the solution in a freezing-mixture of salt and ice, it separated out in a form in which it could be powdered. This operation was repeated twice, and the product analyzed.

0.11051 gram ester gave 0.2514 gram CO_2, and 0.0478 gram H_2O.

	Theory for $C_{18}H_8(COOCH_3)_4$.	Found.
C	62.18	62.05
H	4.66	4.81

This result agrees with the formula for a diphenyltetracarboxylic ester, and to confirm this constitution we isolated the hydrocarbon from which the acid is derived.

A quantity of acid was neutralized with barium hydrate, and the solution evaporated to dryness. The barium salt was intimately mixed with barium hydrate, and the mixture

distilled in a tube, through which a current of hydrogen was passed. The solid hydrocarbon which passed over was crystallized from alcohol, and was shown to be diphenyl.

Although it cannot be regarded as definitely established, the preceding experiments make it probable that both of the products formed in the oxidation of the anhydride, $C_{18}H_{10}O_3$, are diphenyltetracarboxylic acids.

Hydrocarbon from the Anhydride, $C_{18}H_{10}O_3$.

The reduction of the anhydride, through its oxidation product, to diphenyl showed that it must be closely related to this hydrocarbon, and in the expectation that the isolation of the mother-hydrocarbon of the anhydride, and its examination, would give further insight into the nature of the reaction, we turned our investigation in this direction.

Equal weights of the dried barium salt of the acid, $C_{18}H_{12}O_4$, and dehydrated barium hydrate, were quickly heated in a tube, through which a current of hydrogen was passed. A thick oil passed over into the receiver, which was extracted with ether, and the solution shaken out with alkali and dried with calcium chloride. After evaporating the ether a thick oil remained, which weighed about three-fifths as much as the anhydride used. It was fractionated in a vacuum, when almost all of it passed over at 194° (18 mm. pressure, thermometer in vapor). This oil was colored very slightly yellow, but redistillation failed to remove the color.

0.2104 gram oil gave 0.7244 gram CO_2, and 0.1140 gram H_2O.

	Theory for $C_{14}H_{12}$.	Found.
C	93.90	93.90
H	5.79	6.02

The oil has a decided odor of naphthalene, and is readily soluble in glacial acetic acid, but the addition of comparatively little water causes part of the dissolved substance to separate. It is miscible with alcohol only to a moderate extent. The oil did not solidify in a freezing-mixture, and at ordinary pressure it passes over at 326°–327° (corrected 336°–337°).

A molecular weight determination, using glacial acetic acid as solvent, gave 244, while the theory for $C_{14}H_{12}$ is 204.

A comparison of the properties of this hydrocarbon with those given by Möhlau and Berger[1] for α-phenylnaphthalene leave no doubt as to the identity of the two products.

These chemists oxidize their product with potassium permanganate in the presence of caustic soda, to benzoylbenzoic acid, but as we found that this oxidation proceeds slowly, we used chromic anhydride for this purpose. Six grams of oil were dissolved in 50 cc. glacial acetic acid, and 30 grams moist chromic anhydride gradually added in the following manner: One-quarter at first, and the solution slowly heated to 70°, then cooled, and the rest of the chromic anhydride added at once. The solution was heated for three hours at 100°, then the excess of anhydride reduced by addition of alcohol, and the solvent distilled off in a vacuum. The green residue was taken up with water, excess of sulphuric acid added, and the solution extracted with ether. On extracting the ether with caustic potash, and evaporating the solvent, a small amount of a neutral substance, probably an intermediate oxidation product, was left behind. The alkaline solution was then acidified, extracted with ether, and the moist solution left large crystals of pure hydrated benzoylbenzoic acid.

0.1851 gram substance, air-dried, gave 0.4687 gram CO_2, and 0.0840 gram H_2O.

	Theory for $C_6H_5-C(OH)_2C_6H_4COOH$.	Found.
C	68.85	69.06
H	4.92	5.06

The acid melted at 94°, and agreed in its other properties with benzoylbenzoic acid hydrate. In a vacuum it gradually gave off water, and then melted at 120°–125°. A portion was dried at 100° and analyzed.

0.1436 gram acid gave 0.3922 gram CO_2, and 0.0590 gram H_2O.

	Theory for $C_6H_5-CO-C_6H_4-COOH$.	Found.
C	74.34	74.49
H	4.42	4.56

As the calcium, barium, and ammonium salts also agree with those of *o*-benzoylbenzoic acid, there can be no doubt of

[1] Ber. d. chem. Ges., **26**, 1198.

the identity of our product with that acid. We also made an experiment to oxidize the anhydride directly with chromic anhydride, and were able to isolate benzoylbenzoic acid from the products of oxidation, but the yield was very unsatisfactory. Diphenyltetracarboxylic acid is apparently not formed in this way.

Theoretical Considerations.

The conversion of the anhydride into α-phenylnaphthalene and into diphenyltetracarboxylic acid, proves its constitution, but the manner of its formation is open to two different constructions. In the first place, one may assume that a molecule of phenylpropiolic-acetic anhydride is added to the unsaturated fatty carbons of a second molecule, in such a manner that one of the orthohydrogen atoms of the nucleus of the first molecule is added to the α-unsaturated carbon in the side chain of the second molecule, and the negative radical remaining unites with the β-unsaturated carbon, thus giving rise to the following constitution:

$$C_6H_5{-}C{-}C{-}CO{-}O{-}OCCH_3 + C_6H_5{-}C{-}C{-}CO{-}O{-}$$

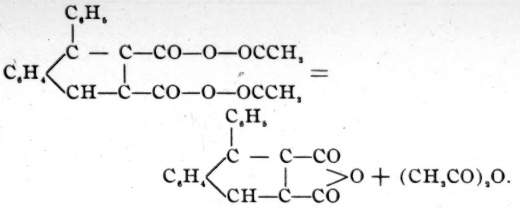
$$OCCH_3 = C_6H_4\begin{cases} C_6H_5 \\ | \\ C{-}CH{-}CO{-}O{-}OCCH_3 \\ C{-}C{-}CO{-}O{-}OCCH_3 \end{cases}.$$

The compound thus formed then undergoes a molecular rearrangement, in which the α-hydrogen of the side chain passes over to the β-carbon of the less saturated side chain, the two α-carbons then saturating each other to form a naphthalene ring:

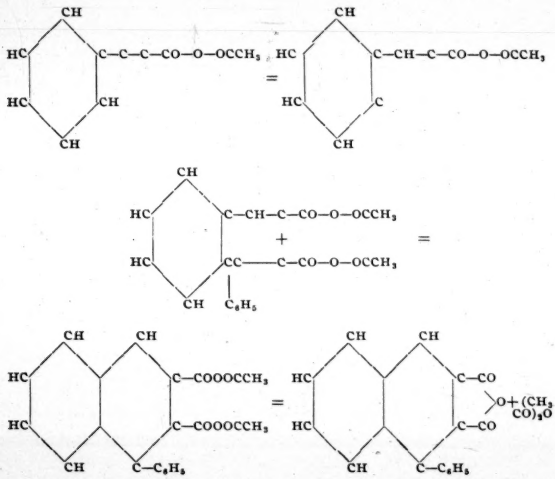
$$C_6H_4\begin{cases} C_6H_5 \\ | \\ C{-}CH{-}COOOCCH_3 \\ C{-}C{-}CO{-}O{-}OCCH_3 \end{cases} =$$

$$C_6H_4\begin{cases} C_6H_5 \\ \diagup \\ C - C{-}CO{-}O{-}OCCH_3 \\ | \\ CH{-}C{-}CO{-}O{-}OCCH_3 \end{cases}.$$

The chain formation is accompanied by the decomposition of the mixed anhydride :

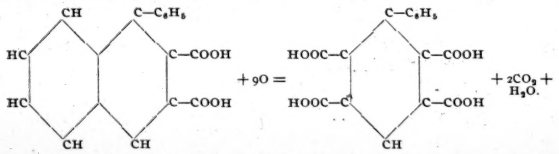


According to the second conception, it may be assumed that an orthohydrogen passes over to the unsaturated β-carbon of the side chain, and this radical then polymerizes with a second molecule of the mixed anhydride :



The substance formed by the action of acetic anhydride on phenylpropiolic acid is therefore the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid, a constitution with which

all the above-described decompositions of the substance are in accordance. It will be shown farther on that the second is the most probable of these two explanations of its formation. By the action of potassium permanganate in alkaline solution the acid corresponding to the anhydride is converted into diphenyltetracarboxylic acid, and a second acid, apparently isomeric with this substance. The formation of the tetrabasic acid may be represented as follows:

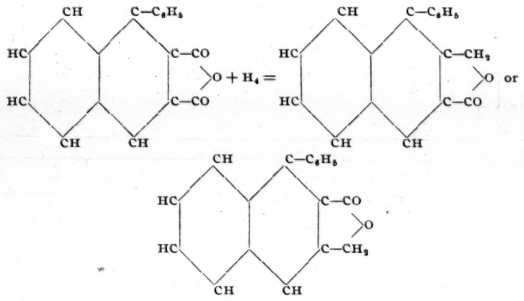


The constitution of the diphenyltetracarboxylic acid therefore follows from that of the naphthalene derivative, and it may be called 1-phenyl-2,3,5,6-benzenetetracarboxylic acid. This constitution agrees with the conversion of the acid into an anhydride, which behavior shows that it contains two pairs of carboxyls, the members of which are in the ortho-position to each other. In regard to the second product of oxidation, it cannot be considered that its constitution as a tetracarboxylic derivate of diphenyl has been conclusively proven; indeed the formation of a second isomeric acid by oxidation of the anhydride is not foreseen by theory. As the substance is undoubtedly a diphenyl derivative, a further investigation of this product is of interest. The formation of diphenyltetracarboxylic acid is peculiar in view of the oxidation of phenylnaphthalene by the same oxidizing agent,[1] or by chromic acid, to orthobenzoylbenzoic acid. It should be remarked, however, that the oxidation with permanganate was finished in acid solution. The behavior of the α-phenylnaphthalene, obtained by us, towards permanganate in presence of alkali, did not agree with the result obtained by Möhlau and Berger, unless it is that in their case the greater part of the oxidation was done in acid solution. A portion of our hydrocarbon was boiled for a long time, in presence of alkali, without much diminution of oil. It would

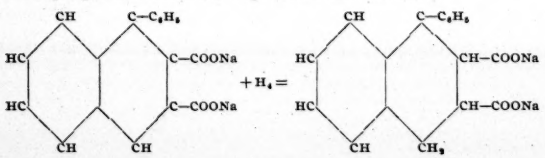
[1] Möhlau and Berger: Ber. d. chem. Ges., **26**, 1199.

seem as if there were some connection between the formation of the tetrabasic acid, when the oxidation takes place in presence of alkalies, and of the less acidic benzoylbenzoic acid, when it takes place in acid solution.

A notable difference occurs also in reducing in alkaline and in acid solution, the hydrogen in the first condition attacking the nucleus, while in the second it acts on a carbonyl. When the anhydride is subjected to the action of hydrogen, the reaction proceeds as in the case of phthalic anhydride, reducing the compound to a lactone, $C_{16}H_{12}O_2$:



Of these two constitutions the former is the more probable, as the most negative carbonyl should be that nearest to phenyl, and it should be first to be reduced. Hydrogen, in acting on the salt of the dibasic acid, may form isomeric compounds, according to whether it attacks the substituted or unsubstituted nucleus. However, all analogy shows that it would be added to the more negative unsaturated carbons, and it may be considered as reasonably certain that the following equation correctly represents the reaction :



The behavior of the unreduced and reduced acids towards permanganate agrees with this constitution, as it has been found that in the case of aromatic acids the reduction of the nucleus invariably makes the product more susceptible to oxidation.

It is a well-known fact that the replacement of the hydrogen in maleïc anhydride increases the stability of the anhydride, so that certain compounds, as dialkyl- or diphenylmaleïc anhydrides, only exist in anhydride condition, the corresponding acids immediately decomposing into anhydrides and water when they are liberated from their salts. This class of anhydrides have hitherto only been known with fatty acids, or aromatic acids in which the carboxyls entering into the anhydride formation form part of the side chain. We have therefore in 1-phenyl-2,3-naphthalenedicarboxylic anhydride, *the first instance of this spontaneous anhydride formation in an acid, in which the carboxyls are directly connected with the aromatic nucleus.* Owing to the lack of experimental material the influence of the alkyl or phenyl on the facility of anhydride-formation of polybasic aromatic acids, which have the carboxyls joined directly to the nucleus, cannot be as definitely traced as in the fatty series, but that this influence is closely related in both series there can be no doubt. Phthalic acid melts at 203°, losing water at that temperature, and passing over into the anhydride; the introduction of methyl in the meta position to both carboxyls, gives an acid that loses water gradually when heated to 100°,[1] and when methyl is introduced into the ortho position to one of the carboxyls the methylphthalic acid formed goes over into its anhydride at 100°, even in the presence of water.[2] Judging by analogy with the fatty series one should expect that an orthodimethylphthalic acid would spontaneously decompose into anhydride and water, but the acid[3] described as such exists in the free state, and does not lose water more easily than the orthomonomethylphthalic acid.[4] Since phenyl favors anhydride-

[1] Von Niementowski: Monatshefte, **12**, 626.

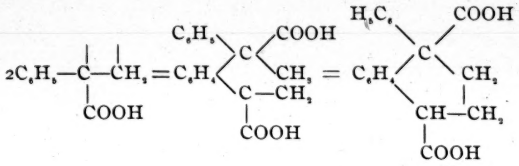
[2] Young: Ber. d. chem. Ges., **25**, 2107.

[3] Gucci and Cristaldi: Centrbl., **62**, II, 548.

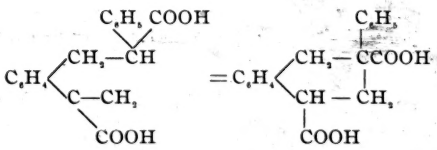
[4] This stability leads one to suspect that the acid may have a different constitution from the one ascribed to it.

formation more than methyl,[1] it is not difficult to understand that our product, which may be considered as derived from phthalic acid by replacing an ortho hydrogen by phenyl and the hydrogen in the meta position to both carboxyls by tetramethylene, should not exist in a free state. There can be no doubt that simpler derivatives of phthalic acid will also show a like behavior.

The synthesis of phenylnaphthalenedicarboxylic anhydride from phenylpropiolic acid is not without analogy, but undoubtedly stands in intimate relation to the formation of the isatropic acids from atropic acid. According to the investigations of Fittig[2] the isatropic acids represent reduced naphthalene derivatives, and their formation may be supposed to take place in a manner exactly similar to the two explanations, which we gave for our substance:



or

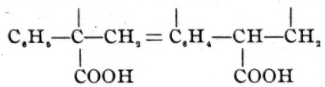


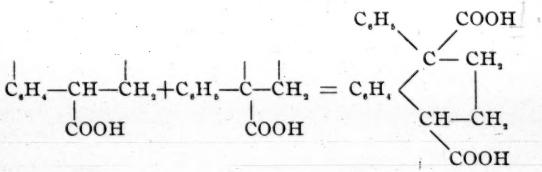
The second of these reactions cannot have taken place, as Fittig proved that the isatropic acids give *o*-benzoylbenzoic by oxidation, and, although it is possible that two molecules of atropic acid unite to form a substance of the constitution represented by the first formula, still it is theoretically very improbable that such a product would easily pass over into the tetrahydronaphthalene derivative, as the hydrogen would

[1] Phenylmaleïc acid loses water with greater ease than does methylmaleïc acid.

[2] Ann. Chem. (Liebig), **206**, 34.

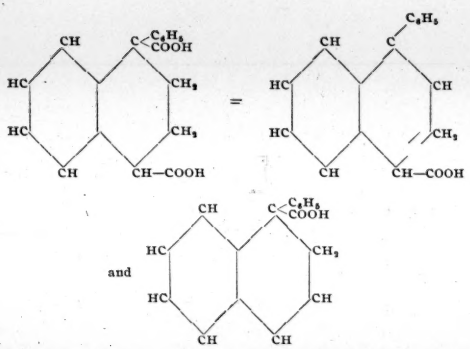
have to leave methyl, and such β-hydrogen shows little tendency to separate from saturated carbon. It is therefore probable that the formation of isatropic acid proceeds by an ortho-hydrogen reducing the adjacent unsaturated carbon of the side chain, and the unstable substance thus formed unites immediately with a second molecule of atropic acid :



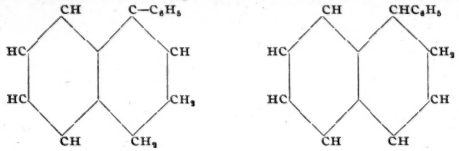


The isatropic acids, considered as reduced naphthalene derivatives, may also be called 1-phenyl-1,4-tetranaphthalenedicarboxylic acids.[1] Chemically related to these acids is tetrahydronaphthalenedicarboxylic acid, which on heating first loses water to form an anhydride, then water and carbon monoxide, passing over into naphthalene. Isatropic acid also loses carbon monoxide and water on heating to form atronic acid, or with concentrated sulphuric acid to form the isomeric isatronic acid. As it is very probable that this decomposition is similar to that of tetrahydronaphthalenedicarboxylic acid, the formation of these acids may be represented as follows :

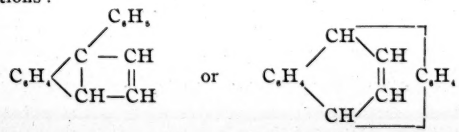
[1] Fittig (Ann. Chem. (Liebig) **206**, 64) also discussed the possibility of the isatropic acids being tetramethylene derivatives, and showed that such a constitution is not in accordance with the formation of benzoylbenzoic acid by oxidation. Liebermann (Ber. d. chem. Ges., **28**, 138), some years later, without any new experimental material, considered the tetramethylene constitution as possible; but that this cannot be the case is evident from the results he obtained in the oxidation of the truxillic acids. The experimental analogy, which Fittig stated as wanting at the time of his work, now exists, and there can be no doubt as to the correctness of the reduced naphthalene constitution, a view which is confirmed by the analogy with the phenylpropiolic acid reaction. We should not have considered it necessary to call attention to this error of Liebermann, if it were not that the obvious mistake of considering isatropic and atropic and truxillic and cumamic acids as standing in the same relation to each other has passed over into a text-book (Richter, Organische Chemie, 7te Auflage, II, 275).



Heated above their melting-points, atronic and isatronic acids give off carbon dioxide, and pass over into the same hydrocarbon which Fittig called atronol. This body is a dihydrophenylnaphthalene, and should possess one of the two constitutions,[1]

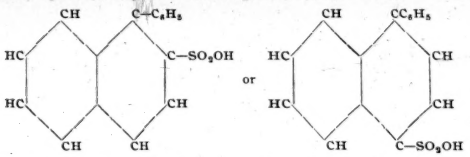


In the decomposition of isatropic acids by sulphuric acid, if the temperature is allowed to rise, a sulphonic acid of a hydrocarbon $C_{16}H_{12}$ is formed. Fittig called the hydrocarbon as atronylene, and suggested for it the following constitutions :

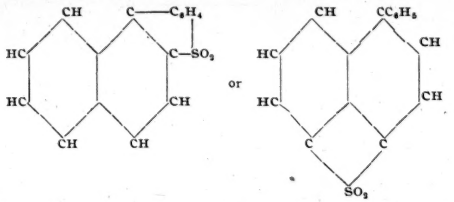


[1] Fittig assigns to atronol the constitution of a 1,4-dihydro-1-phenylnaphthalene. This constitution is not in as close relationship to the atronic acids as those given above, although it is not impossible that such a substance may be formed by molecular rearrangement of the hydrogen in the reduced nucleus. A body having the constitution assigned by Fittig to atronol should be obtained by reduction of α-phenylnaphthalene, and this reaction will be studied.

These interpretations of the reaction are, however, not probable, and there can be little doubt that sulphuric acid acts on isatronic acid in the same manner as it does on isatropic acid, converting it, with the liberation of carbon monoxide and water, into phenylnaphthalene, and the so-called atronylenesulphonic acid is α-phenylnaphthalenesulphonic acid:



The sodium salt of this sulphonic acid shows a remarkable decomposition, losing sodium hydrate, and being converted readily into a sulphone. This is a reaction which as yet has no precedent in organic chemistry, but is probably due to a peculiar atomic arrangement in space causing the phenyl,[1] or the unsubstituted part of the nucleus, to condense with the sulphonoxyl radical:



It is evident that the syntheses of naphthalene derivatives from atropic and phenylpropiolic acids are due to reactions essentially analogous in their nature, and as the second of the possible interpretations of the formation of the isatropic acids is theoretically much more probable than that first stated, it is therefore likely that the phenylpropiolic-acid reaction proceeds in a like manner. In these reactions we have a new procedure, by which certain phenyl derivatives with unsaturated side chains, undergo polymerization with union of carbon atoms to form naphthalene derivatives.

TUFTS COLLEGE, November 1897.

[1] The behavior of α-phenylnaphthalene towards sulphuric acid will be examined in the hope of confirming this view. It is possible, however, that in this case an isomeric sulphonic acid may be formed.

Contributions from the Chemical Laboratory of Harvard College.

THE RELATION OF THE TASTE OF ACIDS TO THEIR DEGREE OF DISSOCIATION.

By Theodore William Richards.

Since no systematic attempt appears to have been made to determine acids quantitatively by means of the sense of taste alone, it seemed worth while to carry out the following series of experiments with this idea in view.[1] The peculiar sourness which is distinctive of acids is probably to be referred to the hydrogen ion, which also is distinctive of them, and it becomes a question of no small interest to determine how closely the taste corresponds to the degree of dissociation.

The sense in question is well known to be rather an uncertain one, depending upon the habits and physical condition of its possessor, so that an experimenter could hardly expect to obtain absolute results from its use. On the other hand, relative taste, determined by alternately tasting two solutions, might well furnish some clue as to the relative strength of these solutions.

The water used in the experiments recorded below was distilled in a platinum still over alkaline permanganate, the first portions of the distillate being rejected. For the final experiments this water was redistilled; in this way an unusually tasteless liquid may be obtained. The solutions of acids, alkalies and salts were carefully made of pure materials. The test was accomplished by simply taking a small mouthful (five cubic centimeters) of the liquid in question, (which is advantageously warmed beforehand to 40°) and allowing this liquid to remain upon the tongue for a few seconds until a constant intensity of taste is secured. A few of the individual experiments are recorded below in order to define the method, but most of them are merely indicated in the conclusions.

(1) To four several portions of water, each measuring 10 cc., were added respectively 0.05, 0.10, 0.20 and 0.30 cc. of decinormal hydrochloric acid. The first of these solutions

[1] Dr. Squibb has used this physiological method upon cocaine with good results. (Ephemeris of Materia Medica, Etc., Brooklyn, N. Y., Vol. III., No. I, p. 918, 1887.) My attention was called to this interesting work after the present paper was written, and I know of no similar investigation.

remained unchanged in taste, the second became faintly acid, and the others very distinctly so.

(2) In order to test the degree of accuracy attainable in this way, a number of beakers containing dilute acid were "shuffled" so that the identity of each was lost, and the attempt was then made to arrange them according to strength by means of the taste alone. Small inconspicuous labels showed finally how successful the attempt had been. In the first trial, four beakers, each containing 30 cc. of water, were acidified by adding 0.2, 0.4, 0.6 and 0.8 cc. of decinormal hydrochloric acid. These were arranged by taste without great deliberation in their proper order, showing that the method is capable of an accuracy of twenty-five per cent., even with a comparatively unpractised tongue.

(3) Another similar trial was made with similar amounts of water containing 0.3, 0.4, 0.5 and 0.6 cc. of decinormal acid respectively. After repeated tasting and much deliberation these were arranged in the order 1, 2, 4, 3; thus my success with the method did not go beyond 20 per cent., although the limit might unquestionably be reduced by practice.

Similar experiments with sulphuric, nitric, and hydrobromic acids showed that the sensitiveness in these cases is about the same—an acid of the concentration of somewhat less than $\frac{1}{1000}$ normal, representing the limit of possible detection as indicated by my sense of taste. This is a very weak solution, containing less than a milligram of hydrogen ions in a litre.

It is, of course, possible that a part of this taste might be due to the negative ion. Further light upon this point is obviously to be obtained by neutralizing the acid with potash or soda. It was found in this way that an acid liquid which tasted distinctly sour became absolutely tasteless upon neutralization; indeed, a centinormal solution of potassium chloride has less taste than a millinormal solution of acid. According to the dissociation hypothesis, the hydrogen ions have been removed by the neutralization, and we are now tasting potassium and chlorine ions, which are either not very strong in taste, or else have the peculiar property of nearly eliminating

one another's taste by mixture. Since most properties of solutions are additive, and we cannot well conceive of a *minus* taste (except such a subtraction from the taste as might be caused by a partial paralysis of the nerves, owing to some very powerful excitement), the former alternative seems to be the most natural one; hence we may believe that neither potassium nor chlorine ions possess as strong a taste as those of hydrogen.

It becomes now a matter of interest to compare these results with those given by very dilute solutions of less ionized acids. Tartaric acid thus diluted, tasted somewhat less sour than a corresponding solution of the mineral acids, citric acid was still less sour, and acetic acid was the least sour of all. While qualitatively these observations agree with those which we should expect to make, the quantitative agreement is less satisfactory. Acetic acid, for instance, seemed to taste at least as strong as hydrochloric acid of one-third its concentration, whereas at a concentration of $\frac{1}{333}$ normal, Kohlrausch's experiments upon its electrolytic conductivity show that only about one-fourteenth of the acid is dissociated.[1] The reason for this discrepancy is not evident, unless the act of tasting removes the dissociated part of the acid and so leaves room for further dissociation, or unless the undissociated acid possesses a taste resembling that of the hydrogen ions, but weaker. Both of these hypotheses carry one too far into physiological chemistry to receive treatment here.

Somewhat more satisfactory were the results of mass action upon the taste. The addition of small amounts of potassic chloride to very dilute solutions of hydrochloric acid produced no appreciable effect upon the taste, while the sourness of acetic acid was noticeably diminished, and that of hydrochloric acid was almost destroyed by adding similar amounts of potassic or sodic acetates. These phenomena are qualitatively in accord with the dissociation hypothesis and the mass law, which tell us that in such a reaction as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

[1] At 18°, when $v = 167$ $\mu = 17.0$
" $v = 500$ $\mu = 28.3$
" $v = \infty$ $\mu = 318.1$
} Weid. Ann., **26**, 161, (1885).

the addition of a large proportion of acetic ions from the almost wholly dissociated sodic acetate is capable of forcing the reaction backwards and destroying the hydrogen ions. The case is of course analogous to the effect of salts in modifying the catalytic action of acids upon cane-sugar and esters, as measured by Ostwald,[1] Arrhenius,[2] Spohr,[3] Trevor,[4] Palmaer,[5] and others. We should expect, however, to find the taste of the acetic acid wholly destroyed by the addition of sodic acetate, because the acid's power of inverting sugar is so much diminished thereby; and the fact that some acid taste remains is only to be accounted for by some such hypothesis as those given above. The fact that the taste of hydrochloric acid is diminished much more than that of acetic acid by the addition of sodic acetate is not inconsistent with these hypotheses; for acetic acid, whether wholly or partly undissociated, has been shown to be much less sour than hydrochloric acid; and acetic acid is undoubtedly formed in this case.

A common application of these principles is to be found in the preparation of the much-used "soda water" or "mineral water" of commerce. Unless a small amount of sodic carbonate is added during its preparation, the effervescent solution is so sour as to be unpleasant to some tastes. This sourness may sometimes have been augmented by a stronger acid carried over in the process of careless preparation; but the fact that it exists in some degree, even in carefully prepared carbonic acid water, was shown by experiment in the laboratory. In any case the sourness is removed by sodic bicarbonate, and the hypothetical explanation is similar to that given above. The following equilibrium is usually assumed to exist in the solution of carbonic acid:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

The acid is, however, only very slightly dissociated. Hydric sodic carbonate, on the other hand, is probably largely dissociated into Na^+ and HCO_3^-, and when this salt is added these latter ions force back the already very slight dissociation of

[1] J. prakt. Chem. (1883), **28**, 449; also (1885) **31**, 307.
[2] Ztschr. physikal. Chem., **4**, 226.
[3] J. prakt. Chem. (1885), **32**, 32.
[4] Ztschr. physikal.Chem., **10**, 321.
[5] *Ibid*, **22**, 492.

the carbonic acid, rendering the solution pleasant and soft to the taste by removing some of the hydrogen ions.

Since sodic chloride was found to possess a taste so much feebler than that of hydrochloric acid, it is evident that the sense of taste might form a fairly sensitive indicator of the end-point of an acidimetric reaction. It is possible easily to detect sourness in a millinormal solution of acid, hence in working with decinormal solutions of acids and alkalies we ought to be able to determine the end-point to within 1 or 2 per cent.

Accordingly several titrations were made with exactly decinormal solutions of hydrochloric acid and sodic hydroxide, the liquid being tasted with a glass rod until the end-point was nearly reached, when small mouthfuls were tasted. The alkalinity of saliva is insufficient to make any essential difference in the results. If large amounts of liquid are removed, it is obviously necessary to allow for the acid or alkali thus taken out; but this correction may be reduced to a very small amount by the use of large quantities of the original solutions.

The best results were obtained by adding slightly too much acid, and then adding alkali until the sour taste just disappeared. The figures are given below—the first and second columns containing the number of cubic centimeters of acid and alkali respectively, and the third the percentage of acid found.

Acidimetric Titration.

Cc. of acid taken.	Cc. of alkali taken.	Per cent. of acid found.
7.00	6.99	99.9
10.73	10.67	99.4
7.21	7.15	99.1
14.96	14.99	100.2
14.44	14.59	100.9
	Average	99.9

The accuracy of these results, which were obtained in an unprejudiced fashion, is somewhat astounding. Evidently, in the course of the few experiments described here, the sense of taste had been noticeably sharpened. To what limit this sensitiveness might be carried, it is hard to predict; but already

the method of analysis had assumed a degree of accuracy exceeding some which are seriously applied as quantitatively useful.

Efforts were made also to analyze the taste produced by weak currents of electricity, as well as the effect of sugars in mitigating the unpleasantness of great acidity of taste, but the complex physiological relations involved in these and similar cases led to an unsatisfactory outcome.

The results of this paper, although they are only qualitatively consistent with the theory of dissociation, nevertheless show that the sense of taste might be used more precisely in the laboratory than is usually believed.

CAMBRIDGE, December 12, 1897.

NOTE ON FEHLING'S SOLUTION.

BY J. BISHOP TINGLE.

M. Z. Jovitschitsch has recently shown[1] that alkaline copper solution, freshly prepared according to Fehling's directions, deposits cuprous oxide either at the ordinary temperature or when heated, if it has been partially neutralized with sulphuric acid, hydrochloric acid, or nitric acid. This result is ascribed to decomposition of the tartrates present in the liquid. It is well known that Fehling's solution slowly undergoes spontaneous decomposition, and the instability of tartaric acid in aqueous solution on exposure to light has been pointed out by W. Seekamp,[2] whilst its oxidation in presence of iron and alkali has been studied by Fenton.[3] Purdy, in his work on "Urine Analysis,"[4] advises, for the determination of dextrose, the use of a solution composed of copper sulphate, potassium hydrate, glycerol, and ammonium hydrate. Since glycerol is much more stable than tartaric acid, it appeared worth while, in view of the intrinsic importance of the subject, to ascertain whether this solution was also affected by the presence of mineral acids. Specimens treated in the manner described by Jovitschitsch, both at the ordinary tempera-

[1] Ber. d. chem. Ges. (1897), **33**, 2431.
[2] Ann. Chem. (Liebig), **278**, 373; also R. Otto: Ber. d. chem. Ges. (1894), **27**, 799.
[3] J. Chem. Soc. (London), 1894, 890; 1896, 546; 1897, 375.
[4] Practical Urine Analysis (3d Edition). F. A. Davis Co., Philadelphia, 1896.

ture and at the boiling-point, gave no sign of reduction. The liquid is very sensitive towards phenylhydrazine, and is readily reduced by lactose, and maltose on heating. The reduction is shown by the weakening or complete discharge of the blue color, and not by the production of a precipitate as in the case of the ordinary Fehling's solution. Purdy's formula for the preparation of the liquid is as follows: Crystallized copper sulphate (4.742 grams) is dissolved in water (200 cc.), and glycerol (38 cc.); potassium hydroxide (23.5 grams) is dissolved in water (200 cc.), the solutions are mixed, ammonium hydrate (sp. gr. 0.9, 450 cc.) is added together with sufficient water to make 1 litre. Of this solution 35 cc. are equivalent to 0.02 gram dextrose. In determining dextrose 35 cc. of the copper solution are diluted with about 2 volumes of water, boiled, and the sugar solution added drop by drop from a burette until the blue color is discharged. The copper solution may be kept for an indefinitely long time without undergoing change.

LEWIS INSTITUTE, CHICAGO, ILL.

ACTION OF THE ANHYDRIDE OF ORTHOSULPHOBENZOIC ACID ON DIMETHYL- AND ON DIETHYLANILINE.

BY M. D. SOHON.

When the anhydride was mixed with dimethylaniline and heated, a green color was developed at about 90°, but the reaction did not proceed to any extent. A similar color was obtained by boiling the mixture in benzene solution for several days. In neither case could the products be separated. Dimethylaniline (2 mols.) was mixed with the anhydride (1 mol.), phosphorus oxychloride added in equal amount, and the mass gently heated on the water-bath, for a short time. Quite an energetic action ensued; the resulting product was boiled with water, when a black tarry mass separated. After cooling, the green supernatant liquid was decanted, and the washing repeated until the wash-water was blue, and the mass solidified on cooling. The wash-waters were examined and found to contain only phosphorus, hydrochloric, and sulpho-

benzoic acids, with some of the green material, the chief product.

Dimethylanilinesulphonphthaleïn,

$$C\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \\ C_6H_4SO_2 \\ O— \end{cases} = C_{22}H_{24}N_2SO_2$$

thus obtained is a blue-black, brittle mass, appearing bright blue in fine powder. Sparingly soluble in cold water, more soluble in hot water, with a bright blue color. Excess of the sulphonphthaleïn in hot water formed a tarry mass which solidified on cooling if pure. It is soluble in alcohol, the solution being precipitated by ether, in which it is insoluble. It is also insoluble in benzene, ligroïn, and chloroform. Analyses gave the following results:

0.4000 gram gave 0.2254 gram $BaSO_4$, equivalent to 7.73 per cent. sulphur.

0.3112 gram gave 0.1781 gram $BaSO_4$, equivalent to 7.80 per cent. sulphur.

0.4121 gram gave 0.0277 gram N, equivalent to 6.72 per cent. nitrogen.

The formula $C_{22}H_{24}N_2SO_2$ requires 7.84 per cent. sulphur and 6.82 per cent. nitrogen.

The aqueous solution of the sulphonphthaleïn dyes silk or wool bright blue. It is more soluble in acids than in water; in dilute acid it dissolves with a green color, becoming yellow on addition of excess of acid. Apparently an unstable salt is formed. On evaporation of the hydrochloric acid solution to dryness, the residue was found to be free from chlorine, and acted like the original material. Neither could any decomposition be effected by boiling with acid. On heating with concentrated hydrochloric acid in a sealed tube, one and a half hours at 180°, decomposition was effected; the material was charred and nothing definite could be obtained.

Phosphorus pentachloride did not act upon it. Heated in a closed tube at 180° the result was similar to that with hydrochloric acid.

Reducing agents failed to act upon the sulphonphthaleïn,

tin, granulated zinc and zinc dust in acid and in alkaline solution, and also sulphites were tried.

The acid or neutral solution, on addition of excess of alkali, becomes pink; the product could not be separated. On removal of the excess of alkali it regained its original color. Nor could change be effected by long boiling. On fusion with potassium hydroxide, empyreumatic odors were evolved and only a carbonaceous residue obtained.

Acetic anhydride did not act upon it, nor bromine in glacial acetic acid solution.

Diethylanilinesulphonphthaleïn,

$$C\begin{cases} C_6H_4N(C_2H_5)_2 \\ C_6H_4N(C_2H_5)_2 \\ C_6H_4SO_2 \\ O— \end{cases} (= C_{31}H_{32}N_2SO_3),$$

prepared in the same manner as the dimethylaniline compound, is similar in its properties. The color was more green.

0.2663 gram gave 0.1315 gram $BaSO_4$, equivalent to 6.78 per cent. sulphur.

0.3112 gram gave 0.1539 gram $BaSO_4$, equivalent to 6.79 per cent. sulphur.

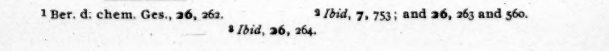
0.1517 gram gave 0.00948 gram N, equivalent to 6.25 per cent.

The formula $C_{31}H_{32}N_2SO_3$ requires 6.89 per cent. sulphur and 6.02 per cent. nitrogen.

THE MOLECULAR WEIGHT OF LACTIMIDE.

By G. M. Richardson and Maxwell Adams.

The α-oxy acids yield neutral anhydrides. In the case of glycolic acid,[1] lactic acid,[2] and α-oxybutyric acid,[3] it has been shown that this dehydration takes place between two molecules of the acid thus:



[1] Ber. d. chem. Ges., **26**, 262. [2] *Ibid*, **7**, 753; and **26**, 263 and 560.

[3] *Ibid*, **26**, 264.

Anhydrides of the higher α-hydroxy acids have not been obtained.

The β-oxy acids lose water and are converted into unsaturated acids:

$$RCHOHCH_2COOH = RCH{=}CHCOOH + H_2O.$$

The γ- and δ-oxy acids lose water when set free from their salts:

$$R{-}CHOHCH_2CH_2COOH = RCH\underset{\llcorner O \text{———} \lrcorner}{\text{—}}CH_2CH_2CO + H_2O$$

and

$$R{-}CHOHCH_2CH_2CH_2COOH = RCH\underset{\llcorner O \text{———————} \lrcorner}{\text{—}}CH_2CH_2CH_2CO + H_2O$$

a reaction which finds a ready explanation when the stereochemical relations of the carbon atoms are considered.

The amido acids also yield neutral anhydrides, apparently in a manner analogous to the oxy acids.

Amidoacetic acid and α-amidopropionic acid both give neutral anhydrides. β-Amidopropionic acid when heated gives acrylic acid and ammonia:

$$CH_2NH_2CH_2COOH = CH_2CHCOOH + NH_3.$$

The γ- and δ-amido acids readily lose water forming the lactames

$$CH_2NH_2CH_2CH_2COOH = \begin{matrix} CH_2CH_2CH_2 \\ | \quad\quad | \\ NH\text{——}CO \end{matrix} + H_2O$$

This analogy between the amido acids and the oxy acids suggests that since the dehydration in the α-oxy acids takes place between two molecules of acid, the dehydration in the α-amido acids also takes place between two molecules.

Curtius[1] attempted to determine the vapor-density of the anhydride of amidoacetic acid in order to decide whether its formula was CH_2NHCO or $(CH_2NHCO)_2$, but without results. Nevertheless he concluded that it must have the doubled formula on account of its high melting-point and its indisposition to take up water and pass back into the amidoacetic acid. Later Curtius and Schultz[1] determined the molecular weight of the anhydride by the freezing-point method and found

[1] Ber. d. chem. Ges., **16**, 755.

the doubled formula to be the correct one. They give $CH_3\langle\begin{matrix}NH—CO\\CO—NH\end{matrix}\rangle CH_3$ as the structural formula.

The only other anhydride of this class thus far described is the anhydride of α-amidopropionic acid or *lactimide* described by Pren.[2] Pren gives to this the formula $CH_3CH\langle\begin{matrix}NH\\|\\CO\end{matrix}$, and this is the formula ascribed to the substance in the chemical literature.

From stereochemical considerations, and by analogy to the oxy acids and especially by analogy to the anhydride of amidoacetic acid, it seems probable that the lactimide of Pren should have the doubled formula and be written

$$CH_3CH\langle\begin{matrix}NH—CO\\CO—NH\end{matrix}\rangle CHCH_3.$$

To test this point experimentally the authors prepared lactimide according to the directions of Pren, and determined its molecular weight by the lowering of the freezing-point of its acetic acid solution. The results show the doubled formula $(CH_3CHNHCO)_2$ to be the correct one.

α-Amidopropionic acid (alanin) was prepared from aldehyde ammonia by the following transformations:

$$CH_3C\begin{matrix}H\\NH_2\\OH\end{matrix} + HCN = CH_3C\begin{matrix}H\\NH_2\\CN\end{matrix} + H_2O.$$

Aldehyde ammonia.

$$CH_3C\begin{matrix}H\\NH_2\\CN\end{matrix} + 2H_2O + HCl = CH_3C\begin{matrix}H\\NH_2\\COOH\end{matrix} + NH_4Cl.$$

Alanin.

Aldehyde ammonia was prepared in the usual manner and dried. A solution of hydrocyanic acid of known strength was prepared by distilling potassium ferrocyanide with sulphuric acid and passing the hydrocyanic acid into distilled water.

The strength of the solution thus formed was determined by saturating 10 cc. of this solution with potassium hydroxide and titrating with standard solution of silver nitrate.

[1] Ber. d. chem. Ges., **23**, 3041. [2] Ann Chem. (Liebig), **134**, 372.

The aldehyde ammonia was dissolved in water and hydrocyanic acid added in the proportions indicated by the equation. To this was added slightly more hydrochloric acid than the equation indicates, and the whole was evaporated until ammonium chloride began to crystallize out. After cooling, the ammonium chloride was filtered out, and washed with a little water; the filtrate, which contains the alanin, was boiled with lead hydroxide to destroy the ammonium salt left in solution, and finally the lead removed from the solution with hydrogen sulphide, and the alanin crystallized from the filtrate.

The dried alanin was placed in a combustion-tube, and dry hydrochloric acid gas passed over it for three hours while it was kept at a temperature of 180° to 200° C. The tarry residue remaining in the tube was boiled with lead hydroxide to free it from hydrochloric acid and any ammonium chloride that might remain. The lead was then removed with hydrogen sulphide, and the lactimide crystallized from the solution. In this manner was obtained a very small yield (about 0.5 per cent. of the theoretical yield) of needle crystals which melt at 271° (uncorrected) and sublime at about their melting-point with slight decomposition.

The substance is extremely soluble in water, soluble with difficulty in glacial acetic acid, and insoluble in absolute alcohol. Pren[1] reports that lactimide is easily soluble in alcohol. The analytical results are given below:

	Found.	Calculated for $CH_3CHNHCO$.
C	50.4	50.70
H	7.2	7.04
N	...	19.72
O	...	22.54

A molecular weight determination by Beckmann's[1] freezing-point method in acetic acid solutions gave the following results:

Weight of acetic acid used as solvent, 20.5473 grams.
Weight of lactimide dissolved, 0.1549 "

[1] Ann. Chem. (Liebig), **134**, 373.

Freezing-point of pure solvent.	Freezing-point of solution.
2.442	2.236
2.440	2.225
2.442	2.225
2.439	....
Mean, 2.441	2.229

Lowering of the freezing-point, 0.212°.

The molecular lowering of the freezing-point for substances dissolved in acetic acid is 38.8. Hence the molecular weight of lactimide is

$$\text{Molecular weight} = \frac{38.8 \times 0.1549 \times 100}{0.212 \times 20.5473} = 137.9.$$

The molecular weight of the formula $CH_3CHNHCO$ is 71, and for the doubled formula $(CH_3CHNHCO)_2$, the molecular weight is 142.

The results of these experiments show that the second formula is undoubtedly the true one.

STANFORD UNIVERSITY, CAL.,
November 18, 1897.

THE ACTION OF SODIUM ETHYLATE UPON α, β-DIBROMHYDROCINNAMIC ESTER, CITRADIBROMPYROTARTARIC ESTER, AND α, β-DIBROMPROPIONIC ESTER.[1]

BY VIRGIL L. LEIGHTON.

The action of sodium ethylate in alcoholic solution upon solid dibromsuccinic ester had been studied by a number of chemists, but owing to the incompleteness and contradictory nature of the results, the subject remained in an unsatisfactory state until recently investigated by Michael and Bucher.[2] It was for the purpose of extending these observations to other similar compounds that the present work was undertaken. The result of the study of dibromsuccinic ester is as follows:

By the action of one molecule of sodium ethylate in alcoholic solution upon sodium succinate, Mulder and Hamberger[3] obtained sodium bromethoxysuccinate, which tested again

[1] The work described in the following pages comprises part of a thesis presented at Tufts College, for the degree of Doctor of Philosophy.

[2] Ber. d. chem. Ges., **28**, 2512; **29**, 1792. [3] Rec. d. trav. chim., **1**, 154.

with sodium ethylate did not give a compound free from bromine as was expected.

Mulder and Wellmann[1] report as the result of the action of potassium ethylate (equal molecules) upon dibromsuccinic ester, bromfumaric or brommaleïc ester. By treatment with two molecules a compound was obtained free from bromine, but, although a number of analyses were made, they were so unsatisfactory that the identity of the product could not be established with certainty.

Pum[2] obtained as the result of the action of equal molecules of sodium ethylate on dibromsuccinic ester, brommaleïc ester, and of two molecules of sodium ethylate to one of ester, acetylenedicarboxylic ester.

Michael and Maisch[3] have shown that the properties and boiling-point of the supposed acetylenedicarboxylic ester obtained by Pum do not agree with those of that compound, and that a compound free from bromine is not obtained by using the theoretical amount of sodium ethylate; but by using an excess of ten per cent. a substance is obtained, which was apparently identical with that of Pum, and which was shown by analysis to be diethoxysuccinic ester.

In a second paper,[4] Pum repeated his former experiments, and stated that he obtained as the product of the action of two molecules of sodium ethylate upon dibromsuccinic ester, a mixture of acetylenedicarboxylic ester and ethoxymaleïc ester, the first ester in relatively small proportion, the acids of which he was able to separate.

Finally, Michael and Bucher[5] have shown that in this reaction an excess of sodium ethylate gives two products, ethoxyfumaric ester (20 per cent.) and unsymmetrical diethoxysuccinic ester (80 per cent.), and that acetylene dicarboxylic ester is not formed even when equal molecules of reagents are used; but the proportions formed of the above esters are reversed. They have also obtained the same products by treating acetylenedicarboxylic ester with sodium ethylate.

The action of sodium ethylate in alcoholic solution has been studied upon a few other similar compounds, namely,

[1] Rec. d. trav. chim., **7**, 334. [2] Monat. f. Chem., **9**, 446.
[3] J. prakt. Chem., **46**, 233. [4] Monat. f. Chem., **14**, 491.
[5] Ber. d. chem. Ges., **28**, 2512; **29**, 1792.

the dibromide of isoeugenol ethyl and methyl ether;[1] anethol dibromide, isosafrol dibromide, and the dibromide of isoeugenol ethyl ether;[2] dibromide of isoeugenol ethyl ether;[3] anethol dibromide and monobromanethol dibromide.[4]

The authors agree that the final product obtained by the action of two molecules of sodium ethylate is a ketone of the following general formula $R.COCH_2CH_3$. This result was explained by Wallach and Pond by supposing that the first action of the sodium ethylate was to split off hydrobromic acid, the ethoxyl radical being then substituted for the second atom of bromine. The product thus formed in contact with water (it was distilled with steam) undergoes hydrolysis, forming an unsaturated carbinol, which being unstable is converted into the ketone. The whole reaction may be represented as follows:

$$R,CHBrCHBrCH_3—HBr = R,CBrCHCH_3;$$
$$R,CBrCHCH_3 + NaOC_2H_5 = R,C(OC_2H_5)CHCH_3 + NaBr;$$
$$R,C(OC_2H_5)CHCH_3 + H_2O = R,C(OH)CHCH_3 + C_2H_5OH;$$
$$R,C(OH)CHCH_3 \rightarrow R,COCH_2CH_3.$$

By allowing one molecule of sodium ethylate to act upon ethylisoeugenol dibromide, Hell and Portmann[5] obtained ethoxyethylisoeugenol bromide,

$$C_6H_3(OCH_3)(OC_2H_5)CH(OC_2H_5)CHBrCH_3,$$

which, when heated, or distilled under 15 mm. pressure, loses alcohol and yields the compound

$$C_6H_3(OCH_3)(OC_3H_4)CHCBrCH_3.$$

The authors conclude, therefore, that the first action is not to split off hydrobromic acid, but that the bromine atom in the α-position to the benzene ring is first substituted by the ethoxyl radical, then hydrobromic acid splits off, and subsequent hydrolysis gives the ketone thus:

$$R,CHBrCHBrCH_3 + NaOC_2H_5 = R,CH(OC_2H_5)CHBrCH_3 + NaBr$$
$$R,CH(OC_2H_5)CHBrCH_3—HBr = R,C(OC_2H_5)CHCH_3$$
$$R,C(OC_2H_5)CHCH_3 + H_2O = R,C(OH)CHCH_3 + C_2H_5OH$$
$$R,C(OH)CHCH_3 = R,COCH_2CH_3$$

[1] Hell and Portmann: Ber. d. chem. Ges., **28**, 2088.
[2] Wallach and Pond: *Ibid.*, **28**, 2714. [3] Hell and Portmann: *Ibid.*, **29**, 676.
[4] Hell and Hollenberg: *Ibid.*, **29**, 682. [5] *Ibid.*, **29**, 676.

The Action of Sodium Ethylate upon α,β-Dibromhydrocinnamic Ester.

The α,β-dibromhydrocinnamic ester used in the following experiments was prepared from cinnamic acid by first converting it into the ester, which was then dissolved in an equal volume of carbon tetrachloride, and the calculated amount of bromine added slowly from a drop funnel in the sunlight, the mixture being kept cool by a bath of ice-water. The carbon tetrachloride was allowed to evaporate, at first spontaneously, then in a vacuum, and finally the remaining oil was sucked out with a pump, and the product washed with a little absolute alcohol and dried. It melted at 67°–68°.

To 10 grams of dibromhydrocinnamic ester suspended in an equal weight of absolute alcohol was added drop by drop a solution of sodium ethylate, made by dissolving 1.5 grams of sodium (theory for two molecules 1.37 grams) in 20 grams of absolute alcohol, the temperature being kept below 6°. Sodium bromide began to separate immediately. After standing six days, it remained alkaline to litmus. It was then saturated with carbon dioxide, the sodium bromide and carbonate separated by filtration and the excess of alcohol distilled off in a vacuum upon the water-bath. A little water was then added to the residue, the supernatant oil separated, shaken out with a solution of sodium carbonate, and dried over calcium chloride. The product contained considerable bromine (detected by the cupric oxide test) from which repeated distillation failed to free it entirely.

To get a product free from bromine 10 grams of the dibromhydrocinnamic ester, treated as before with ten per cent. excess of sodium ethylate, was allowed to stand three days at the ordinary temperature, then boiled two and a half hours on the water-bath. The solution was then neutral, so that 0.15 gram more sodium dissolved in alcohol was added and the solution again boiled two hours. It then remained strongly alkaline. The product worked up as before gave on distillation an oil free from bromine.

This experiment, repeated with 73 grams of dibromhydrocinnamic ester, gave 47 grams of crude product free from bro-

mine. Three grams of phenylpropiolic acid, which crystallized from hot water in characteristic crystals, melting at 136°, was obtained from the sodium carbonate solution by acidulating with sulphuric acid and extracting with ether.

The neutral oil was repeatedly fractioned (with beads) in a vacuum and finally two products were obtained, one boiling at 146°–148° at 10 mm. pressure (metal bath 180°), and a much larger portion boiling at 154°–155° at 9 mm. pressure (bath 185°). The former product will be described later; the latter gave the following results on analysis:

0.2141 gram of substance gave 0.554 gram of carbon dioxide and 0.142 gram of water.

	Calculated for ethoxycinnamic ester.	Found.
C	70.80	70.56
H	7.30	7.38

It was therefore ethoxycinnamic ester.

β-Ethoxycinnamic Acid.

The ethoxycinnamic ester obtained as above was saponified very slowly by a dilute solution of caustic potash at ordinary temperature. It was therefore boiled with a very slight excess of a four per cent. aqueous solution of caustic potash, in a flask with a return-condenser. After complete solution, which required about one and a half hours, it was acidulated with sulphuric acid, when nearly pure ethoxycinnamic acid was precipitated as a voluminous, white crystalline solid, which, dried in a vacuum over sulphuric acid, melted at 158°–160° with decomposition. From carbon tetrachloride it crystallized in thin, transparent, well-formed crystals, which, dried over sulphuric acid in a vacuum, melted with decomposition at 164°–165°, and gave the following analytical results:

0.255 gram of substance gave 0.642 gram of carbon dioxide, and 0.1455 gram of water.

	Calculated for ethoxycinnamic acid.	Found.
C	68.73	68.65
H	6.26	6.38

The ester, dissolved in a little alcohol, was treated with concentrated hydrochloric acid (sp. gr. 1.2), and evaporated

in a vacuum over sulphuric acid and caustic soda. The residue was again treated with hydrochloric acid, evaporated, and this process repeated until the saponification seemed complete. At the end of the operation the characteristic odor of acetophenone was noticeable. The residue, a white crystalline solid, was dissolved in hot benzene and a few drops of ligroïn added, when benzoylacetic acid separated out in well-defined crystals. The yield was 85 per cent. of the theoretical. Dried in a vacuum over sulphuric acid it melted with decomposition at 102°–103° (Perkin[1] gives 104°). The decomposition-point was found to depend to some extent upon the rapidity of heating. The analysis gave the following results:

0.1582 gram of substance gave 0.3814 gram of carbon dioxide, and 0.0766 gram of water:

	Calculated for $C_6H_5COCH_2COOH$.	Found.
C	65.85	65.80
H	4.91	5.38

Heated to 110° it decomposed into carbon dioxide and an oil, which was insoluble in alkalies, and had the characteristic odor of acetophenone. It gave with phenylhydrazine a crystalline hydrazone, melting at 105° (characteristic of acetophenone).

The ethoxycinnamic acid obtained above was treated like the ester with hydrochloric acid, and the same product, benzoylacetic acid, was obtained. Crystallized from benzene and ligroïn, it decomposed at 102°–103°, and gave the following results on analysis:

0.1456 gram of substance gave 0.351 gram of carbon dioxide, and 0.0698 gram of water.

	Calculated for $C_6H_5COCH_2COOH$.	Found.
C	65.85	65.74
H	4.91	5.33

It has been shown[2] that ethoxyfumaric and ethoxymaleïc esters are converted into oxalacetic acid by saponification with aqueous hydrochloric acid. This is explained by supposing

[1] J. Chem. Soc. (London), **45**, 170.

[2] Michael and Bucher: Ber. d. chem. Ges., **28**, 2512; **29**, 1792.

that the hydroxyfumaric or hydroxymaleïc acid is first formed, which then goes over into the saturated acid as follows:

$$\begin{array}{l} HC{-}COOC_2H_5 \\ | \\ H_5C_2OC{-}COOC_2H_5 \end{array} \rightarrow \begin{array}{l} HC{-}COOH \\ | \\ HOC{-}COOH \end{array} = \begin{array}{l} H_2C{-}COOH \\ | \\ OC{-}COOH. \end{array}$$

The action of hydrochloric acid upon ethoxycinnamic ester or acid in a similar way may be represented as follows:

$$C_6H_5C(OC_2H_5)CHCOOC_2H_5 \rightarrow C_6H_5C(OH)CHCOOH = C_6H_5COCH_2COOH.$$

It is therefore β-ethoxycinnamic acid.

β-Ethoxycinnamic acid is a white, crystalline solid, almost insoluble in cold water, soluble in alcohol, sparingly soluble in ether, slightly soluble in cold and easily in hot carbon tetrachloride and benzene, insoluble in cold ligroïn. It crystallizes from solution in carbon tetrachloride, or when a solution of its salt is acidulated, in thin, transparent, truncated prisms, which melt with decomposition at 164°–165°.

The silver salt, made by treating the ammonium salt with silver nitrate, is formed as a white crystalline mass, which under the microscope appears in the form of fine needles. The air-dried salt does not lose weight when heated to 100°. Dried in a vacuum at 100° it gave the following analytical results:

0.2132 gram of substance gave 0.0766 gram of silver.

	Calculated for $C_6H_5C(OC_2H_5)CHCOOAg$.	Found.
Ag	36.09	35.94

The calcium salt crystallized from a moderately concentrated solution in white needles (the crystallization is greatly facilitated by boiling the solution), which air-dried gave the following results on analysis:

0.201 gram of salt gave 0.0479 gram of calcium sulphate.

	Calculated for $[C_6H_5C(OC_2H_5)CHCOO]_2Ca,8H_2O$.	Found.
Ca	7.07	6.98

The water of crystallization was not determined directly as the salt began to decompose before all the water was expelled.

The copper salt is crystalline and slightly soluble in water. The lead and zinc salts are also slightly soluble.

Diethoxyphenylpropionic Ester.

The first portion of the distillate, obtained by treatment of dibromhydrocinnamic ester with sodium ethylate (page 136), owing to the small quantity of substance and slight decomposition on distillation could not be entirely purified by fractionation. It gave the following results on analysis:

0.2038 gram of substance gave 0.5158 gram of carbon dioxide, and 0.1444 gram of water.

	Calculated for $C_6H_5C(OC_2H_5)_2CH_2COOC_2H_5$.	Calculated for $C_6H_5C(OC_2H_5)_2CHCOOC_2H_5$.	Found.
C	67.63	70.80	69.01
H	8.33	7.30	7.87

It was therefore evidently a mixture of the two esters.

A small quantity saponified with a four per cent. solution of caustic potash in ninety per cent. alcohol, by standing in the cold, gave on acidulating with sulphuric acid, benzoylacetic acid, which, crystallized from benzene and ligroïn decomposed at 102°–105° into carbon dioxide and acetophenone.

To show that benzoylacetic acid is not formed by saponification of ethoxycinnamic ester by aqueous potash in the cold, a small portion of this ester was treated with a slight excess of a four per cent. solution of aqueous caustic potash, and allowed to stand with occasional shaking, for two weeks, at ordinary temperature. It finally nearly all went into solution. Acidified with sulphuric acid, ethoxycinnamic acid separated as before; recrystallized from carbon tetrachloride and dried in a vacuum over sulphuric acid, it melted with decomposition at 163°–164°.

The formation of benzoylacetic acid is explained in the same way as the formation of oxalacetic acid from ethoxyfumaric ester.[1] It has been shown[2] that in alcoholic solution unsymmetrical diethoxysuccinic acid is first formed, which when heated is decomposed to oxalacetic acid, and not, as Nef supposed, saponifying directly to hydroxyfumaric acid. In the above case unsymmetrical β-diethoxyphenylpropionic

[1] Nef: Ann. Chem. (Liebig), **276**, 226.

[2] Michael and Bucher: Ber. d. chem. Ges., **28**, 2512; **29**, 1792.

ester should first be formed, which, being unstable under the conditions of the experiment, would be decomposed to benzoylacetic acid.

The above-mixed esters, saponified with aqueous hydrochloric acid, gave pure benzoylacetic acid.

Pure ethoxycinnamic ester, treated with sodium ethylate (1 mol.) in an equal weight of absolute alcohol, allowed to stand at ordinary temperature five days, and worked up as usual, gave a mixture of the two esters similar to the original mixture, boiling at 130°–135° at a pressure of 2–2.5 mm. (bath 150°) without decomposition, and gave the following results on analysis:

0.1424 gram of substance gave 0.3638 gram of carbon dioxide, and 0.1063 gram of water.

	Calculated for $C_6H_4C(OC_2H_5)_2CH_2COOC_2H_5$.	Calculated for $C_6H_5C(OC_2H_5)CHCOOC_2H_5$.	Found.
C	67.63	70.80	69.59
H	8.33	7.30	8.22

The Action of Sodium Ethylate upon Citradibrompyrotartaric Ester.

The citradibrompyrotartaric ester used in the following experiments was made from citraconic anhydride, by first converting it into the ester, which distilled at the ordinary pressure at 228°–230°. To this ester, dissolved in an equal volume of carbon tetrachloride, the calculated amount of bromine was added slowly in the the direct sunlight, the mixture being cooled by ice-water. It was allowed to stand a short time in the sunlight, then washed with water and sodium carbonate solution, dried over calcium chloride, the carbon tetrachloride distilled off, and the residue fractionated. The final product boiled constant at 160°–161° under a pressure of 20 mm.

To 20 grams of citradibrompyrotartaric ester, dissolved in an equal weight of absolute alcohol, was added gradually from a drop funnel 2.66 grams (theoretical amount) of sodium dissolved in 36 grams of absolute alcohol. The temperature was kept below 20°. Sodium bromide began to separate out immediately. The solution was allowed to stand sixty-six hours, and at the end of that time it was slightly alkaline. It

was then saturated with carbon dioxide, the sodium bromide and carbonate removed by filtration, the alcohol distilled off in a vacuum on the water-bath, water added and the supernatant oil separated. The aqueous solution was extracted with ether and the etherial solution added to the oil. The whole was then shaken out with a solution of sodium carbonate, and dried over calcium chloride. The ether was distilled off on the water-bath, and the product (9 grams) fractionated in a vacuum. All the fractions contained considerable bromine, which a refractionation failed to remove. It was therefore necessary to use more than the theoretical amount of sodium. To determine this another preliminary experiment was made.

To 20 grams of citradibrompyrotartaric ester in an equal weight of absolute alcohol was added, in the same way as before, 2.96 grams of sodium (theory 2.66) dissolved in 40 grams of absolute alcohol. It remained only slightly alkaline, so 0.3 gram more sodium dissolved in alcohol was added, and the solution allowed to stand several days. It remained strongly alkaline. Worked up as before the crude product showed the presence of bromine, but was freed from it by fractionation.

From 168 grams of ester treated in this way with twenty per cent. excess of sodium ethylate, 87 grams of a neutral oil was obtained. There was also extracted by the sodium carbonate solution, and obtained from this by acidifying with sulphuric acid and extracting with ether, 21 grams of an oil having acid properties. This was not further investigated. The neutral oil was purified by repeated fractionation in a vacuum (with beads), and finally two products were obtained, one boiling constantly at 140° under a pressure of 15 mm. (bath 170°), and the other, a somewhat larger portion, at 157° under the same pressure. The former product gave the following analytical results:

I. 0.1712 gram of substance gave 0.3586 gram of carbon dioxide, and 0.1336 gram of water.

II. 0.1714 gram of substance gave 0.3598 gram of carbon dioxide, and 0.1336 gram of water.

	Calculated for Ethoxycitraconic ester.	Found. I.	II.
C	57.38	57.12	57.24
H	7.84	8.68	8.67

The above ester saponified by a four per cent. solution of caustic potash in the cold, the solution, acidified and extracted with ether, gave on distilling off the ether a thick viscous oil, which, allowed to stand in a vacuum over sulphuric acid in the cold for a long time, did not solidify. An analysis gave the following results :

0.1356 gram of substance gave 0.2412 gram of carbon dioxide, and 0.0733 gram of water.

	Calculated for Ethoxycitraconic acid.	Found.
C	48.28	48.50
H	5.75	6.01

The ester treated with concentrated hydrochloric acid did not give oxalpropionic acid as was expected. Boiled with a ten per cent. solution of sulphuric acid it gave carbon dioxide and propionylformic acid, which treated with phenylhydrazine gave the characteristic hydrazone, melting at 148°–149°[1]. On analysis this gave the following results :

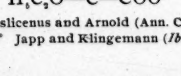
0.1248 gram of substance gave 0.2894 gram of carbon dioxide, and 0.073 gram of water.

	Calculated for $C_2H_5C(N_2HC_4H_3)COOH$.	Found.
C	63.54	63.24
H	6.35	6.50

The salts of ethoxycitraconic acid are very soluble in water, except those of lead and silver. The barium salt can be precipitated with alcohol. An analysis of the salt obtained in this way, and purified by repeated precipitation, gave results as follows :

0.1755 gram of air-dried substance lost, at 100°, 0.0103 gram (= 5.86 per cent. H_2O), and gave 0.1328 gram $BaSO_4$ (= 44.51 per cent. Ba).

Calculated for



Per cent.

H_2O = 5.98

Ba = 44.34

[1] Wislicenus and Arnold (Ann. Chem. (Liebig), **246**, 333) found the melting-point 144°–145.° Japp and Klingemann (*Ibid*, **247**, 216) found it 152°.

The higher-boiling portion of the original product (157° at 15 mm.) gave the following analytical results :

0.1828 gram of substance gave 0.3772 gram of carbon dioxide, and 0.1453 gram of water.

	Calculated for Diethoxypyrotartaric ester.	Found.
C	56.50	56.33
H	8.71	8.85

Saponified with dilute caustic potash in the cold, acidifying and extracting with ether, the ethereal solution dried over calcium chloride, the ether partially distilled off on the water-bath, and the remainder in a vacuum over sulphuric acid, it gave a thick oil which failed to solidify on standing. Analyzed without further purification it gave the following results:

0.1848 gram of substance gave 0.3336 gram of carbon dioxide, and 0.1200 gram of water.

	Calculated for Diethoxypyrotartaric ester.	Found.
C	49.09	49.23
H	7.27	7.21

The silver salt is a white crystalline compound, nearly insoluble in water. It does not lose weight at 100°. The analysis of the salt, dried at 100°, resulted as follows :

0.109 gram of substance gave 0.0543 gram of silver.

	Calculated for $C_8H_{12}O_6Ag_2$.	Found.
Ag	49.77	49.81

Thelead salt is also nearly insoluble in water ; all the other salts made were very soluble, and the barium salt can be evaporated to a syrup without crystallization. The ester saponified by repeated treatment with concentrated hydrochloric acid gave the same product as that saponified with caustic potash. The silver salt of the acid obtained in this way, made by treating with silver nitrate in acid solution, filtering off the small quantity of silver chloride, and neutralizing the filtrate with ammonium hydroxide, gave the following analytical results :

0.063 gram of substance gave 0.0312 gram of silver.

	Calculated.	Found.
Ag	49.77	49.52

The ester boiled with a 10 per cent. solution of sulphuric acid did not give propionylformic acid.

The ethoxycitraconic ester obtained above, dissolved in alcohol, treated again with sodium ethylate (1 mol.) and worked up as usual, gave a mixture of ethoxycitraconic ester and diethoxypyrotartaric ester similar to the original mixture, which could be separated by distillation.

The Action of Sodium Ethylate upon α,β-Dibrompropionic Ester.

The dibrompropionic ester used in these experiments was made from allyl alcohol by adding bromine in a solution of carbon bisulphide, in the sunlight, the solution being cooled by a bath of ice-water, the carbon bisulphide was distilled off and the product purified by fractionation in a vacuum, the final product distilling at 102°–104° at a pressure of 13 mm. (bath 140°). This product was oxidized with nitric acid, and the resulting dibrompropionic acid crystallized out by cooling, washed with nitric acid, and crystallized from ligroïn. It melted at 62°–63°. It was converted into the ester in the usual way.

To 5 grams of the ester dissolved in an equal weight of absolute alcohol, 1 gram of sodium (theory 0.88 gram) in 13 grams of absolute alcohol was added, the temperature being kept below 10°. After standing eight days it was worked up as in the preceding cases. The product contained considerable bromine which could not be removed by fractionation.

10 grams of the ester treated in the same way with 2 grams of sodium (theory 1.76 grams) in 25 grams of absolute alcohol was allowed to stand three days, and then boiled two hours on the water-bath. It became nearly neutral; 0.2 gram more sodium dissolved in alcohol was added, and the solution again boiled two hours. It then remained alkaline; the product worked up as before contained a trace of bromine, which was removed by distillation. 40 grams of the ester treated in this way with an excess of 20 per cent. of sodium gave 13 grams of the neutral oil, and 5 grams of an oil having acid properties was obtained from the sodium carbonate solution

by acidifying with sulphuric acid and extracting with ether; the last product was not investigated.

The neutral oil fractionated in a vacuum began to distil at about 65° under a pressure of 9 mm., the temperature rising gradually to 150°. It was evidently a mixture of two or more substances, and owing to the small quantity of the material at our disposal it was impossible to separate the constituents entirely by fractionation. However, after several distillations, a small quantity was obtained boiling from 64°–65° at 9 mm., which on analysis gave the following results:

0.1925 gram of substance gave 0.4057 gram of carbon dioxide, and 0.1533 gram of water.

	Calculated for ethoxyacrylic ester.	Calculated for diethoxypropionic ester.	Found.
C	58.33	56.84	57.47
H	8.33	9.47	8.84

The analysis therefore indicates that it was a mixture of these two compounds.

Conclusion.

A 20 per cent. excess (over 2 molecules) of sodium ethylate in alcoholic solution acts upon α,β-phenyldibrompropionic ester to form mostly β-ethoxycinnamic ester, with a small quantity of unsymmetrical diethoxyphenylpropionic ester. The reaction may take place in the following stages:

I. $C_6H_5CHBrCHBrCOOC_2H_5 - HBr = C_6H_5CHCBrCOOC_2H_5$;

II. $C_6H_5CHCBrCOOC_2H_5 + C_2H_5OH = C_6H_5CH(OC_2H_5)CHBrCOOC_2H_5$;

III. $C_6H_5CH(OC_2H_5)CHBrCOOC_2H_5 - HBr = C_6H_5C(OC_2H_5)CHCOOC_2H_5$;

IV. $C_6H_5C(OC_2H_5)CHCOOC_2H_5 + C_2H_5OH = C_6H_5C(OC_2H_5)_2CH_2COOC_2H_5$.

Or the first atom of bromine may be replaced directly as follows:

$C_6H_5CHBrCHBrCOOC_2H_5 + NaOC_2H_5 = C_6H_5CH(OC_2H_5)CHBrCOOC_2H_5$,

the reaction then taking place as in III and IV.

Unsymmetrical diethoxyphenylpropionic acid is unstable, decomposing and forming benzoylacetic acid.

There was also a small quantity of phenylpropiolic acid formed in this reaction, due probably to the saponification of the ester, and the inability of the salt to take up sodium ethylate by addition.

A twenty per cent. excess (over 2 molecules) of sodium ethylate in alcoholic solution acts upon citradibrompyrotartaric ester to form ethoxycitraconic ester, and, in considerably larger quantity, diethoxypyrotartaric ester. The reaction may be represented as follows:

$$\begin{array}{l} CH_3CBrCOOC_2H_5 \\ \quad | \\ HCBrCOOC_2H_5 \end{array} + 2NaOC_2H_5 = \begin{array}{l} CH_3C{-}COOC_2H_5 \\ \quad\quad | \\ \quad\quad C(OC_2H_5)COOC_2H_5 \end{array} + 2NaBr + HOC_2H_5;$$

$$\begin{array}{l} CH_3CCOOC_2H_5 \\ \quad | \\ C(OC_2H_5)COOC_2H_5 \end{array} + C_2H_5OH = \begin{array}{l} CH_3C(OC_2H_5)COOC_2H_5 \\ \quad\quad | \\ HC(OC_2H_5)COOC_2H_5. \end{array}$$

There are two possibilities for the constitution of the last compound. Its behavior towards phenylhydrazine, dilute sulphuric, and hydrochloric acids makes it very probable that it has the symmetrical constitution as given above.

Unsymmetrical diethoxysuccinic acid reacts with phenylhydrazine like oxalacetic acid.[1] Boiled with a 10 per cent. solution of sulphuric acid pyruvic acid is formed.[1] Saponified with hydrochloric acid oxalacetic acid is produced.[2]

The diethoxypyrotartaric acid obtained from the above ester does not react with phenylhydrazine hydrochloride. Boiled with a 10 per cent. solution of sulphuric acid it undergoes decomposition, but does not form propionylformic acid. The ester saponified with hydrochloric acid in the cold gives the same product as that saponified by caustic potash. It is

[1] Michael and Bucher, communicated by the authors.
[2] Michael and Bucher: Ber. d. chem. Ges., **29**, 1792.

therefore very unlikely that it is the unsymmetrical compound.

The experiments with α,β-dibrompropionic ester were so unsatisfactory that no conclusions could be drawn from them.

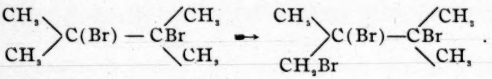
TUFTS COLLEGE, November, 1897.

Contributions from the Sheffield Laboratory of Yale University.

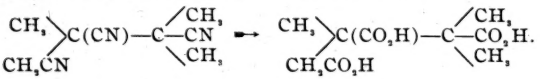
LVII.—ON SOME BROMINE DERIVATIVES OF 2,3-DIMETHYLBUTANE.

BY H. L. WHEELER.

Theoretically by the action of one molecule of bromine on tetramethylethylene bromide, or, 2,3-dibrom-2,3-dimethylbutane, 2,3,K[3]-tribrom-2,3-dimethylbutane should result as follows:



It being immaterial which hydrogen is substituted, only one tribromide would result. Such a compound would be interesting on account of the possibility of converting it into the nitrile of camphoronic acid and this into the acid:



2,3-Dibrom-2,3-dimethylbutane is now readily prepared from pinacone by the methods of Baeyer[1] and Thiele.[2]

However, the action of one molecule of bromine on this compound, which is attacked with exceptional ease, does not give a tribromine compound, but, instead, a tetra derivative results and a corresponding amount of the material remains unaltered.

Linnemann[3] states that when isobutyl bromide is acted on by bromine, no trace of a dibromide is obtained, but a tribromide results exclusively. Linnemann's experiments were conducted at 150°. The author has found that, when this compound is brominated in the presence of iron, the reaction

[1] Ber. d. chem. Ges., **26**, 2563. [2] *Ibid*, **27**, 455.
[3] Ann. Chem. (Liebig), **162**, 34.

takes place readily on the steam-bath, and a dibromide results, although the yield is poor and the reaction is by no means as smooth as with ethyl and propyl bromides. This dibromide is apparently 1,2-dibrom-2-methylpropane. This result suggested the possibility of obtaining the tribromhexane by the use of iron. 2,3-Dibrom-2,3-dimethylbutane was therefore brominated with iron in carbon tetrachloride, but it was found that a tetrabromide results in this case also.

The product obtained without the use of iron melted constantly at 123° when crystallized from alcohol or ether. When, on the other hand, iron was present, a product melting at 139° was obtained. It was found later, by using carbon tetrachloride as a solvent, that the material melting at 123° was impure and that it contained material melting at 139°–140°, and also a compound melting much higher. It was also found that a mixture of 2,3-dibrom-2,3-dimethylbutane melting at 192°, and the tetrabromide melting at 139° melts at about 123°. It is certain that the same tetrabromide results in both of the above cases. The products had apparently the same solubility and the crystals were identical in appearance.

Bouchardat[1] obtained a tetrabromine derivative from iodhexylene by the action of bromine. This iodhexylene was prepared from pinacone hydrate and hydrogen iodide. He assigns the melting-point 142° to this compound.

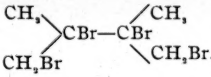
It is probable that Bouchardat's product, melting at 142°, and that of the author, melting at 139°, are identical, especially since in both cases the same compound would be expected.

Mariuza[2] prepared a tetrabromhexane from di-isopropenyl, (2,3-dimethyl-1,3-butadiën) and bromine. This, Beilstein[3] states, melts at 131°, and Couturier[4] confirms the preparation of a crystalline tetrabromide from this compound but does not state its melting-point.

By the action of alcoholic potassium hydroxide on 2,3-dibrom-2,3-dimethylbutane the author has obtained an oil, (2,3-dimethyl-1,3-butadiën) which on adding bromine gave a tetrabromide. This, on crystallizing from alcohol and ether, did not melt at 131° but at 139°. From the method of prepa-

[1] Compt. rend., **74**, 810. [2] Jour. Russ. Chem. Soc., **21**, 435.
[3] The original article is inaccessible to me. [4] Bull. Soc. Chim. (Paris), [3], **4**, 30.

ration it is concluded that this is identical with Mariuza's compound. It is identical in every respect with the product obtained by brominating 2,3-dibrom-2,3-dimethylbutane. Therefore this compound, the only tetrabromide of 2,3-dimethylbutane known at present, is 2,3,K^2,K^3-tetrabrom-2,3-dimethylbutane and its structure is as follows:



(M. P. 139°).

Experimental Part.

2,3-Dibrom,2,3-dimethylbutane, $(CH_3)_2CBr—CBr(CH_3)_2$.—This was prepared by the method of Baeyer by saturating a glacial acetic acid solution of pinacone with hydrogen bromide, or by adding pinacone to hydrogen bromide solution saturated at 0° according to Thiele's directions. In both cases the product, on crystallizing from alcohol, melted at 192° or thereabouts. There being some discrepancy in the statements regarding the melting-point of this compound, a bromine determination was made with the result given below. Pawlow[1] states that the compound melts at a temperature higher than 140°, Beilstein credits Eltekow[2] with the statement of 140° as its melting-point, and Kaschirsrky[3] 169°–170°, while Baeyer and Thiele do not mention its melting-point. Couturier[4] states that it melts at 171° in a closed tube, and Kondakow[5] says that on keeping, the melting-point is reduced to 140°. This shows the influence that a slight impurity has on the melting-point of the substance.

A bromine determination in a product prepared by Thiele's method, which melted at about 192°, gave the following:

	Calculated for $C_6H_{12}Br_2$.	Found.
Br	65.6	65.4

2,3-Dibrom-2,3-dimethylbutane, on being mixed with one molecular proportion of bromine, evolves a slow but steady stream of hydrogen bromide. After a number of hours, when the bromine practically disappears, the material washed with

[1] Ann. Chem. (Liebig), **196**, 124. [2] Jour. Russ. Chem. Soc., **10**, 220.
[3] *Ibid*, **13**, 84. [4] Ann. Chem. et Phys., [6], **26**, 433.
[5] J. prakt. Chem., **54**, 431.

alcohol and crystallized from ether and alcohol—which removes some compound which attacks the eyes—melts then at 123°. A bromine determination gave:

	Calculated for $C_6H_{10}Br_4$.	Found.
Br	79.6	79.1

From ether, on spontaneous evaporation, beautiful minute prisms separated. These seemed to leave little doubt of the purity of the substance, but, on crystallizing from carbon tetrachloride the melting-point finally rose, and there was obtained a small amount of a substance crystallizing in needles and melting—not sharply—at 162° (Unaltered material?). From the mother-liquor, on standing, needles and granular, stout prisms separated. The latter melted at 139°–140°.

Owing to the difficulty of purifying the material obtained in the above manner, attention was directed to the bromination in the presence of iron. This proceeds in a smoother manner and more rapidly.

2,3,K²,K³-Tetrabrom-2,3-dimethylbutane. — This was obtained when 25.0 grams of 2,3-dibrom-2,3-dimethylbutane (1 molecule), 0.5 gram iron wire and 18.0 grams of bromine (1 molecule + 1.4 grams Br for $FeBr_2$) were mixed in carbon tetrachloride. The mixture on warming begins to evolve hydrogen bromide, and then further warming is unnecessary. In a short time all the bromine disappears, and this compound separates in granular crystals melting at 139°. [Analysis I.]

2,3-Dimethyl-1,3-butadiën, $CH_2=C(CH_3)-C(CH_3)=CH_2$. —An attempt was made to prepare 3-brom-2,3-dimethyl-1-butene, $(CH_3)_2CBrC\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}$, by the action of one molecule of alcoholic potassium hydrate on the dibromide. The mixture was boiled until it was no longer alkaline. It was then cooled, when unaltered dibromide separated, melting at 192°. The alcohol was distilled off and water was added to the distillate. This gave an oil which was dried over calcium chloride and distilled. The first and larger fraction boiled from 65° to 80° and contained only a small amount of bromine, the remainder from 80° to 160°. When bromine was added to these fractions, in glacial acetic acid, an immediate precipitate of the

tetrabromide melting at 139° was obtained. It was obtained in larger amount from the lower-boiling fraction. From the fact that the potassium hydroxide was neutralized in the above boiling, and that considerable unaltered material remained, it is concluded that this fraction is chiefly 2,3-dimethyl-1,3-butadiën, and that alcoholic potassium hydrate extracts 2 molecules of hydrogen bromide from 2,3-dibrom-2,3-dimethylbutane. This is confirmed by the fact that a tetra- and not a tribromide is obtained with bromine. A bromine determination in the case of the material melting at 139°, thus obtained, gave the following result: [Analysis II.]

	Calculated for $C_6H_{10}Br_4$.	Found. I.	Found. II.
Br	79.6	79.5	80.0

1,2-Dibrom-2-methylpropane, $(CH_3)_2CBr—CH_2Br$.— When isobutyl bromide is warmed on the steam-bath with iron and bromine, in the proportion to form a dibromide, the reaction is complete in a short time. On washing the product with water and dilute sodium hydrate, an almost colorless oil was obtained. This dried over calcium chloride boiled from about 110° to 214°. On fractioning, a portion was obtained boiling from 146° to 151°, mostly between 148° and 149° *i. e.*, the boiling-point of 1,2-dibrom-2-methylpropane. A bromine determination gave 70.8 per cent. bromine instead of 74.0 per cent. required for a dibromide. This material is therefore mostly 1,2-dibrom-2-methylpropane. From this it will be noticed that bromine in the presence of iron, acts on isobutyl bromide in the same manner as bromine acts on isobutyl iodide. Linnemann[1] states that in the latter case the yield is also poor.

When 2,3-dibrom-2,3-dimethylbutane was boiled with a slight excess of potassium hydrate, in alcoholic solution, an oil was obtained. This was dried over calcium chloride and inadvertently distilled over sodium. On adding bromine to the fraction boiling from 69° to 85°, *i. e.*, the larger fraction, a curious result was obtained. Regenerated 2,3-dibrom-2,3-dimethylbutane separated, melting at about 192°. This low-boiling fraction must, therefore, have contained 2,3-dimethyl-2-butene, which boils at 73°, $(CH_3)_2C=C(CH_3)_2$. This suggests that

[1] *Loc. cit.*

2,3-dimethyl-1,3-butadiën, $CH_2=C(CH_3)-C(CH_3)=CH_2$, on partial reduction, does not give 2,3-dimethyl-1-butene, $(CH_3)_2CH-C(CH_3)=CH_2$, but, that a rearrangement takes place giving the above isomeric hydrocarbon. At present the lack of material prevents a further investigation of this subject.

NEW HAVEN, CONN., December, 1897.

PHOSPHATIC CHERT.

BY J. H. KASTLE, J. C. W. FRAZER AND GEO. SULLIVAN.

One of the most characteristic formations in central Kentucky is a deposit of chert which might be called the Lower Hudson chert. This chert marks the upper boundaries of the Trenton limestone and is so persistent and characteristic that it has proven one of the surest guides in the determination of this particular geological horizon. A remarkable feature of the Trenton limestone of Kentucky immediately underlying this deposit of chert is the presence, in the upper portion of it, of thin strata of highly phosphatic limestone, usually of a light brown color. Several years ago Dr. Robt. Peter, chemist of the Kentucky Geological Survey, called attention to these layers of phosphate in our limestone as the probable cause of the remarkable and enduring fertility of the soil of the Blue Grass section of this state.[1] Dr Peter made numerous analyses of the phosphatic limestone from several localities and found them to contain from 1.46 to 31.815 per cent. of phosphoric acid, P_2O_5, the average being about 15.9 per cent. Our attention was again called to these deposits of phosphate in the Trenton by the recent discoveries of workable quantities of phosphate rock in about the same formation near Nashville, Tenn.; and on the May Farm near Lexington, Ky., J. C. Frazer found an outcrop of phosphate rock about 2½ ft. in thickness, and in the soil of the ploughed field immediately overlying this deposit the Lower Hudson chert was found in abundance. In view of the close proximity of the Lower Hudson chert to the phosphatic limestone it occurred to one of us, Mr. Geo. Sullivan, to examine the former for phosphoric acid, with the result that it was invariably found to be present. Since this first observation a great many specimens of this chert have been collected from the following localities

[1] Reports of the Geological Survey of Ky., Chemical Analysis, A., pt.2, p. 184.

in Fayette Co., *viz:* The grounds of the State College of Kentucky, the May Farm, the Frazer Farm, along the line of the Lexington and Eastern R. R., along the line of the Queen and Crescent R. R., from Athens, Ky., and from Fayette Co., near Clarke.

These specimens from these different localities and even from the same locality, have been found to vary quite considerably in color, texture, and hardness. Some of the specimens were found to be hard and flinty, having a conchoidal fracture and in color varying from white to lead-gray or brown; other specimens were white in color, soft and very much like pure clay in appearance; by far the greater number of specimens collected, however, had the appearance of sand-rock and also of being very much weathered. These varieties of the substance varied considerably in color also, passing from almost white through various shades of light brown to dark reddish-brown.

Under the microscope most of the specimens exhibited a honeycomb or cellular structure,—the walls of the cavities being composed for the most part of glassy quartz. The microscopic cavities of the rock were also found to contain a reddish substance closely resembling red clay; probably ferric phosphate. This, however, was usually present only in small amounts. Many of the specimens of chert were found to be fossiliferous, containing fossils characteristic of the Lower Hudson. The chert from the several localities was analyzed with the following results:

Table I, Chert from Lower Hudson.

No. of specimen.	Per cent. P_2O_5.	Per cent. insol. matter.	Description of specimen.
1	0.261	94.43	Like sandstone, color light brown.
2	1.48	88.0	Like sandstone, color light brown.
3	0.217	97.32	Like sandstone but of loose texture. Contains some few fossils.
4	1.64	86.63	About the color of ferruginous clay; matrix of silica easily seen by unaided eye.
5	0.179	96.60	Like sandstone, color light buff, compact.
6	1.054	92.34	Fossiliferous, color light buff, streaked with dark brown; compact.

No. of specimen.	Per cent. P_2O_5.	Per cent. insol. matter.	Description of specimen.
7	1.05	88.24	Large specimen, about 100 lbs. in weight, dark brown portion.
8	0.57	96.22	From same specimen as No. 7, light portion.
9	0.526	96.4	From same specimen as 7 and 8. The light silicious-looking portion.
10	1.39	88.01	Dark in color, porous, from College grounds.
11	0.965	89.87	Color brown, porous.
12	1.39	76.15	Light-colored silicious specimen.
13	2.8	....	Porous, dark; specimens from College grounds.
14	3.		
15	3.		
16	3.5		
17	2.		
18	2.1		
19	0.6	....	Hard flinty chert; small pieces.
20	0.8	....	Clayey chert.
21	2.	....	Very hard white chert.
22	1.42	....	Hard, flinty chert.
23	3.5	....	Very porous and greatly weathered, filled with cavities, spongy in appearance. Color dark-brown.
24	2.	....	Porous, ferruginous, yellowish brown.
25	2.3	....	Mottled dark-brown and white.
26	2.1	....	Light-colored, porous variety.
27	2.5	....	Hard, white and flinty.
28	1.4	....	Dark brownish-gray, porous.
29	2.6	....	Brown and porous.
30	2.8	....	Brown and very porous.
31	2.8	....	Large, light-brown chert, shaped like a bone.
32	2.5	....	Very hard chert, darker in center, found in nodular-shaped masses.
33	1.75	....	Very thick, hard, massive block of chert.
34	0.2	....	White variety, containing shells of gastropoda.
35	0.5	....	Very hard massive chert, light-colored.
36	1.5	....	Light reddish brown in color.
37	1.3		
38	2.5		
39	1.5		

These results certainly show that phosphoric acid while small in amount is a persistent and characteristic constituent of the chert of the Lower Hudson formation, varying from 0.179 to 3.5 per cent. of P_2O_5. The average of these analyses is 1.684 per cent. of P_2O_5. As the result of numerous analyses, Dr. Robt. Peter found the average amount of phosphoric acid in the Trenton limestone of Kentucky other than the thin phosphate strata already mentioned to be 0.414 per cent. of P_2O_5[1] and in 32 of the soils overlying the Trenton limestone this same chemist found an average of 0.328 per cent. of P_2O_5[2], and in a few remarkably fertile soils of this locality still larger amounts of phosphoric acid, ranging from 0.492 to 0.53 per cent. and to 0.604 per cent. have been observed. It would thus seem that the Lower Hudson chert contains about four or five times as much phosphoric acid as either the soil or limestone rock of these localities, but a considerably smaller amount than the phosphate rock proper of the upper Trenton. Chert from other localities, *viz.*, from the birdseye (or Highbridge) limestone in Kentucky and from the Permian in Russia, has been examined and found to contain phosphates.

Table II, from Birdseye Limestone.[3]

No. of specimen.	Per cent. P_2O_5.	Description of specimen.
1	3.	White, fossiliferous chert, darker in color on surface.
2	0.75	Very hard compact chert with layer of brown, porous, middle portion.
3	0.5	Very hard, white, massive chert.
4	0.25	Hard, light-brown chert with dark porous surface.
5	0.3	Very hard chert, containing layer of dark spongy substance.

The origin and geological history of chert is still obscure; and whether this phosphate is original to it or of secondary origin is still an open question. Certain facts would seem to

[1] Reports of the Geological Survey of Kentucky, Chemical Analyses, pt. 2, Table 1, p. 129.

[2] Reports of the Geological Survey of Kentucky, Chemical Analyses, pt. 2, Table B, p. 113.

[3] The specimen of Russian chert was from the Permian, and was furnished by Prof. Miller. It was in the form of a nodule, interior flinty, and contained only traces of phosphoric acid.

point to one conclusion and some to another. The following facts, however, have certainly a bearing upon this problem: First, two specimens of this chert have been found in direct association with the limestone of this formation, that is, as parts of the same rock fragment. In one of these the limestone formed the central portion of the specimen with the chert on the outside. The specimen had a fresh appearance and neither the limestone nor the chert seemed to have been weathered in the least. The chert in this specimen was found to contain 1.36 per cent. of P_2O_5 and 84.92 per cent. insoluble silica or silicates, whereas the limestone center contained only 0.767 per cent. of P_2O_5 and 42.78 per cent. insoluble residue and 56 per cent. carbonate of lime. The results obtained in the case of this specimen would seem to point to the conclusion that the phosphate is an original constituent of the chert; secondly, that the chert had been formed at the same time and by essentially the same process as the limestone; and, thirdly, that there was a gradual passage from limestone to chert: the large amount of insoluble residue in the limestone of this specimen would certainly seem to justify this last conclusion. A second specimen of this chert in intimate association with the limestone, and forming part of the same specimen, was found by A. M. Miller, Professor of Geology in the State College of Kentucky, in a quarry a few miles from Lexington. This specimen consisted of a light gray chert and a lower layer of ordinary limestone and gave the following results on analysis:

	P_2O_5. Per cent.	Insoluble silicates. Per cent.
Cherty portion,	0.34	90.32
Limestone,	0.31	4.06

While this particular specimen shows only a small amount of phosphate it would seem to indicate that it is as characteristic and original with the chert as with the limestone. Further, there is a tradition among certain of the farmers of this locality that those fields in which the chert is found most abundantly are by far the most fertile. This chert may be only the sign and not the cause of this fertility, however, for as has already been observed the phosphate rock of

the Trenton is usually found in intimate association with this chert and hence the increased fertility of these soils may in reality have resulted from the weathering of the phosphate rock. On the other hand, it should be mentioned in this connection that those cherts which have the appearance of having been most weathered have been found almost invariably to contain the largest amounts of phosphates. Further, it has been observed that specimens having the darkest color and containing the largest quantities of iron contain also the largest quantities of phosphoric acid. It is rather difficult to account for this difference in the amount of phosphate in the weathered and unweathered varieties of chert. It has been suggested to us that it has filtered into the chert from the soil, and hence that the phosphate is of secondary origin. This of course may be true, but in the light of our present knowledge it is rather difficult to see anything in the nature of the chert that would cause this concentration of the phosphate. In view of its intimate association with the great deposits of limestone, it would seem more probable that the pores of this chert had once been filled with calcium carbonate containing phosphates, the latter possibly in the form of fossil remains: and that the former having been weathered out by exposure have left the phosphate in relatively larger amount than that contained in the unweathered chert. Another interesting occurrence of phosphoric acid in this locality which has been discovered in connection with the investigation of the Lower Hudson chert, is a chert breccia which has been found in considerable quantities in the beds of several of our smaller streams. It was first found in several ploughed fields underlying the Lower Hudson chert. This chert breccia is dark brown in color, and is composed of fragments of hard, flinty chert, some worn and rounded and others sharp and angular and cemented together by a dark brown material (probably impure phosphate of iron) containing small acicular crystals of manganese dioxide. Pieces of this substance have been found varying in size from one to two inches in diameter to masses a foot or two across and weighing from one to two hundred pounds.

Specimens, 36, 37, 38, and 39 in Table I. were found along the banks of one of the small streams, in the bed of which oc-

curred large quantities of chert breccia. These pieces of chert had evidently been weathered out of the breccia by the running water. The dark brown cementing material, which often composes quite a large proportion of the entire specimen, is rich in phosphate. The three specimens analyzed gave the following numbers:

	Insoluble silicates. Per cent.	P_2O_5. Per cent.
I.	46.66	4.38
II.	46.58	4.47
III.	44.62	4.5
IV.	....	3.0

We have recently heard of a locality in which the Lower Hudson chert probably occurs in place; and if this should prove to be the case further studies of this rock will be undertaken. Still other geological formations in this state contain extensive deposits of chert, and these also will be examined for phosphate. The occurrence of phosphates in a silicious material such as chert, is rare and interesting, and may eventually throw light on the origin of this peculiar geological formation.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
December, 1897.

ON THE EFFECT OF LIGHT ON THE COMBINATION OF HYDROGEN AND BROMINE AT HIGH TEMPERATURES.

BY J. H. KASTLE AND W. A. BEATTY.

The combination of hydrogen and chloride to form hydrochloric acid has been, and is still, the subject of a great deal of investigation. The effect of light, especially on this combination, has been very thoroughly studied by Draper, Bunsen and Roscoe, and others. In this connection it has been observed by Amato that a mixture of hydrogen and chlorine, if cooled to -12° C., could be exposed to direct sunlight for hours without combination taking place. Such being the case it occurred to one of us (Kastle) that sunlight ought to cause the combination of hydrogen and bromine, or at least accelerate the change of these elements into hydrobromic

acid, if the temperature be raised sufficiently to enable them to combine at all. So far as could be discovered, no studies of this kind had ever been undertaken. It is stated, however, that hydrogen and bromine do not combine at ordinary temperatures even in the sunlight. In order, therefore, to determine the effect of light on this reaction, a number of glass bulbs were made out of a long piece of glass tubing, in such a way as to leave one bulb connected with another in series by means of a short glass tube of small bore. Hydrogen was then passed through the series of bulbs, and, after they had been filled with the gas, the hydrogen was allowed to bubble through a small quantity of bromine, which had been purified by distillation over sodium bromide, and thus saturated with bromine, it was passed through the bulbs. In this way the bulbs were filled with hydrogen more or less saturated with bromine vapor. The most remote necks of the end bulbs of the series were then sealed off in the flame of the blow pipe; and a series of bulbs thus obtained each of which contained very nearly, if not exactly, the same quantities of hydrogen and bromine. Each bulb was then sealed off in such a way as not to allow any of the gases to escape. The exact amount of hydrogen and bromine, in the bulbs, was not determined; it is known, however, that hydrogen was always present in excess. The hydrogen used in the experiments of series Nos. I. and II., was only purified by passing the gas through potassium permanganate and water; whereas the hydrogen employed in the experiments of series No. III. was very carefully purified by using a little copper sulphate in the sulphuric acid employed in making the gas, and by passing the gas through a solution of copper sulphate, then through one containing potassium permanganate, then through water and a solution of silver nitrate, and finally through pure water. Further, the hydrogen employed in all of the experiments herein described was not dried but used moist. Judging from certain preliminary experiments, it was thought best to work at temperatures in the neighborhood of 200° C.; and *o*-toluidine boiling at 196° C. was selected as a suitable medium in which to heat the bulbs, the manner

of conducting the experiments being about as follows:

The bulbs containing the mixture of hydrogen and bromine were placed in large, thin-walled glass tubes, containing about 50 cc. of *o*-toluidine, and so arranged as to be mainly in the vapor of the boiling toluidine and not in the liquid itself. The large glass tubes were closed with corks bearing a long piece of glass tubing, to serve as a reflux condenser. Some of the bulbs, thus arranged, were heated in the dark, and some in the sunlight. Only bulbs of the same series, of course, were compared as to the effect of light, and the amount of change was measured by the alteration in the color of the bromine.

The following are the results of three series of experiments:

Series No. 1. Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	1 hour.	Sunlight.	Change nearly complete, only slight color of bromine remaining.
2	2 hours.	Dark.	Very slight, if any difference in color of bromine. Very little change.
3	½ hour.	Sunlight.	Color intermediate between 1 and 2. About ½ bromine combined.

Series No. II. Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	95 minutes.	Sunlight.	Nearly complete.
2	5 hours.	Diff'd light.	Color intermediate between 1 and 3, this series. About half the bromine combined.
3	3 hours.	Dark.	Color about as deep as in unexposed bulbs. Very little, if any, change.

Series No. III. Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	15 minutes.	Sunlight.[1]	Over 50 per cent. of bromine combined.
2 Same bulb as used in (1)	30 minutes.	Sunlight.	Almost complete—only traces of bromine left.
3	1 hour.	Dark.	No change observable.
4 Same bulb as used in (3)	15 minutes.	Sunlight.	About 50 per cent. change.
5 Same bulb as used in (3) and (4)	15 minutes.	Sunlight.	Intermediate in color between (4) and (6).
6[2] Same bulb as used in (3), (4), and (5)	15 minutes.	Sunlight.	Change nearly complete; only traces of bromine remaining.

These results certainly go to prove that light causes the combination of hydrogen and bromine, at 196° C., the amount of change being proportional to the time of exposure to light. In the dark, at 196° C., the combination of these two gases is exceedingly slow, whereas, in the sunlight, the change is fairly rapid at this temperature. Further, certain results which have been obtained would seem to indicate that light causes the combination of these elements even at 100° C.; although further experiments will be necessary in order to fully establish this point.

[1] The bulbs used in the experiments of Series No. III were the only ones exposed to strong sunlight. During the time of the experiments of Series I. and II., the sky was frequently overcast by thin, white clouds, so that the exposures to the direct sunlight were frequently interrupted.

[2] The bulb used in experiments 3, 4, 5, and 6, was opened and tested for hydrobromic acid. On opening the bulb, dense, white fumes appeared. A little water was run into the bulb and the solution thus obtained gave the well-known reactions of hydrochloric acid.

Further, the results herein described serve to strengthen the analogy existing between chlorine and bromine; and the difference in the temperatures necessary to enable the light to cause the combination of these elements with hydrogen is simply another rough measure of their relative affinity.

A more extended investigation of this subject will be undertaken, and exact measurements made of the rate of this change, at different temperatures, in the light and in the dark. The influence of light on the combination of hydrogen and iodine, at high temperatures, will also be studied.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Dec., 1897.

CHRISTIAN WILHELM BLOMSTRAND.

The Professor of Chemistry and Mineralogy in the University of Lund, Sweden, Christian Wilhelm Blomstrand, died on the 5th of November in his seventy-first year. He began and completed his studies in the University with which he was connected at the time of his death. Three years after he was awarded the degree of Doctor of Philosophy he became assistant to the Professor of Chemistry, and in 1854 he was made instructor. Later he became Professor of Chemistry and Mineralogy, and, after forty years' service, he resigned in 1895 for the purpose of devoting his time to investigation. His name is well known in connection with a large number of investigations in different fields of chemistry, and on account of the originality of the views put forward by him in his book entitled "Chemie der Jetztzeit vom Standpunkte der elektrochemischen Auffassung aus Berzelius' Lehre entwickelt." He did a good deal of work on the rarer metals, as, for example, molybdenum, tungsten, tantalum and niobium, and on many of the complex and rare minerals found in Norway and Sweden, as, for example, monazite, xenotim, ilmenite, tantalite, niobite, etc. One mineral of this group is called Blomstrandite in honor of him.

Among the most interesting of his purely chemical articles is that on the oxygen acids of iodine, in which it was clearly shown for the first time that these acids can be most satisfactorily explained by assuming that in them the iodine is poly-

valent, and that the valence reaches a maximum of 7 in periodic acid. It was shown that the complex periodates could be explained by making this assumption in regard to the valence of iodine, and the view, which was then taken by Blomstrand and seemed startling to timid chemists, has become familiar and is probably quite generally accepted.

Blomstrand also interested himself to a large extent in the diazo compounds, and pointed out a number of years ago that the commonly accepted view is not as satisfactory as another, according to which these compounds appear as ammonium derivatives containing a trivalent and a quinquivalent nitrogen atom. One result of the recent heated discussion between Hantzsch and Bamberger has been to make it clear to the rest of the chemical world that Blomstrand's view is altogether the most satisfactory one. In the last number of the Journal für praktische Chemie, there is an article by Blomstrand on this subject in which he takes the part of Bamberger, and expresses his own ideas with considerable emphasis.

In addition to being an active investigator and a prolific writer, Blomstrand was a teacher of unusual power.

I. R.

REVIEWS.

PRECIS D' ANALYSE CHIMIQUE. PREMIÈRE PARTIE, ANALYSE QUALITATIVE, DEUXIEME PARTIE, ANALYSE QUANTITATIVE. Par E. FINK. Georges Carré et C. Naud. Paris. 1896.

This work, which is divided into two parts, a qualitative and quantitative volume, is evidently intended for the use of practical chemists or of persons who have not had a scientific chemical training, so the information given in these books is of such a nature and so arranged as to serve (to a considerable extent) as a guide to one unskilled in chemical manipulation. In the qualitative part, after giving a list of the necessary reagents, and their method of preparation, the metals are taken up in turn, according to their arrangement in groups, and a list of their insoluble compounds given, with the equations expressing the formation of these compounds and some of their characteristics, in most cases, however, only the color. This is followed by a similar method of procedure in the case of the insoluble salts of the acids, both inorganic and organic, and the usual methods for the separations of the groups and

members of the groups. While on the one hand the book is a mere compendium and of little use to a scientific student of chemistry, on the other hand the matter is presented in such a way as probably hopelessly to bewilder the uninitiated. A general idea of the contents of the volume on quantitative chemistry can be gotten from the table of contents, the six chapters being devoted to the following subjects: Description of apparatus used in quantitative analysis; General operations of quantitative analytical chemistry; Classification and determination of the metals; Separations of the metals; Determination and separation of the acids; and Elementary organic analysis.

In the chapter devoted to methods for the determination of the metals, the members of the different groups are taken up in order, and several methods are given for each one. These methods are, however, described very briefly, and in many cases no attempt is made to explain the chemical reaction upon which the method is based. There are of course many persons engaged in practical chemical work, who have been trained to do the work in a mechanical way, and the skill and knowledge gained in this way may enable them to use this book with success. J. E. G.

INTRODUCTION TO ELECTRICAL CHEMICAL EXPERIMENTS. By DR. FELIX OETTEL. Translated (with the author's sanction) by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Philadelphia: P. Blakiston, Son & Co. 1897. 144 pp.

A brief notice of the German edition of this book appeared in this Journal last year (Vol. XIX, p. 622). To what was there said it need only be added that the translation will be welcomed by English-speaking students. The translator is well known in connection with the subject of electrochemistry, and we may therefore assume that he has done his work well. This subject is being developed so rapidly that the time may be said to have come when it is necessary for all students of chemistry to familiarize themselves with the methods in use in that subject. This book will furnish teachers with directions for a comparatively simple and yet sufficiently full course of experimental work for their students, and it is desirable that work of this kind should be introduced into our laboratories as soon as possible. I. R.

RECUEIL DE PROCEDES DE DOSAGE. Par G. ARTH, Professeur de Chimie Industrielle a la Faculté des Sciences de Nancy. Carré et Naud: Paris. 1897.

This book, as the author remarks in the introduction, is not a text-book of analytical chemistry, but only a collection of the specially valuable methods used in the industrial estab-

lishments of France and some others which he has culled from different sources. The subject is treated under three main heads: Analysis of fuel; Analysis of rocks; and Analysis of iron, cast iron, and steel. The methods of analysis and determination of the various factors, which are necessary to determine the value of fuels, are given both for solid fuels, as wood, coke, coal, and related substances, and also for gaseous ones, as blast-furnace gases. The section devoted to mineral analysis gives the methods used for the determination of the different constituents in minerals containing iron; while the last part is devoted to methods for the determination of the carbon, in different forms, phosphorus, silicon, and other constituents of cast-iron and steel. The arrangement of the book is systematic, and the subject is treated in a very compact but thorough manner. The methods are especially selected for their rapidity and accuracy, and in some cases, as the author says in the introduction, a rapid method is given, and also another to act as a check on the more rapid one. The book will no doubt prove valuable to any chemist interested in furnace work and the chemical processes taking place there. J. E. G.

NOTE.

To the Editor: The great success of the Second International Congress of Applied Chemistry leads us to the belief that the next one, which is to be held in Vienna in July, 1898, will also be numerously attended. Nearly 2,000 members were present at the Paris meeting, and it required five large volumes to contain the report of its proceedings.

The undersigned have been appointed a committee in the United States, to promote the interests of the Third International Congress of Applied Chemistry and beg to call the attention of the chemists of this country to that meeting, with the hope that many may be induced to attend. Those who subscribe and receive their membership cards will be entitled to all reductions in rates going to and coming from Vienna, which are arranged for members of the Congress. During the Paris meeting, the French line of steamers reduced its rates 33 per cent. to members of the Congress. It is hoped that an arrangement can be made with some of the steamship lines during the coming summer for a similar reduction, although

the committee has not yet been informed of any arrangement of this kind.

The opportunity of meeting distinguished chemists from all parts of the world should not be lost sight of, and will doubtless be appreciated by the American members. The scientific work of the Congress will be divided into the following sections:

Section 1.—General analytical chemistry and apparatus, Dr. George Vortmann, Wien, IV Schaumburgergasse 16, chairman.

Section 2.—Food, medicinal and pharmaceutical chemistry, Dr. Ernst Ludwig, Wien, XIX Bilrothstrasse 72, chairman.

Section 3.—Agricultural chemistry, Prof. E. Meissl, Wien, II Trummerstrasse 3, chairman.

Section 4.—Chemistry of the sugar industry, Prof. Friedrich Strohmer, Wien, IV/2 Schönburgstrasse 6, chairman.

Section 5.—Chemistry of the fermenting industries, Prof. F. Schwackhäfer, Wien, XIX Karl Ludwigstrasse 74, chairman.

Section 6.—Chemistry of wine-making, Dr. L. Rosler, Wien, Physiologische Versuchsstation, chairman.

Section 7.—Inorganic chemical industries (manufacture of sulphuric acid, soda, etc.), Herr Paul Seybel, Wien, III Reissnerstrasse 50, chairman.

Section 8.—Metallurgy and explosives, Prof. Franz Kupelwieser, Wien, I Franzenring, chairman.

Section 9.—Organic chemical industries, Dr. Hugo Ritter von Perger, Wien, IV Gusshausstrasse 23, chairman.

Section 10.—Chemistry of the graphic industries (photochemistry, photography, etc.), Dr. Josef Maria Eder, Wien, VII West Cohnstrasse 25, chairman.

Section 11.—Didactic chemistry, Prof. Franz Lafar, Wien, Technische Hochschule, chairman.

Section 12.—Electrochemistry, Dr. Karl Kellner, Hallein, Salzburg, chairman.

All persons desiring to become members, and wishing further information on the subject of the Congress can secure copies of the provisional *reglement* by addressing the Chairman of the Committee, Washington, D. C.

Excursions, visits to localities of interest, banquets, etc., will be arranged for and definitely announced at a later period. Papers in German, French, and English will be accepted, and authors are requested to communicate with the several chairmen, and send them titles of papers and subjects which they would like to have discussed.

All persons intending to become members of the congress may receive a membership card from the secretary, Dr. F. Strohmer, by sending 21 francs to his address, IV/2 Schönburgstrasse, Nr. 6, Vienna, Austria. If preferred, members may send $4.30 to the Chairman of the American Committee who will transmit the proper amount to Dr. Strohmer.

The provisional officers of the Congress are as follows:

President of Honor—Hofrath Prof. Dr. Alexander Bauer.

Active President—Regierungsrath Dr. Hugo Ritter v. Perger, Professor in the Royal Imperial Technical High School of Vienna.

Vice-President—Regierungsrath Dr. Josef Maria Eder, Director of the Royal Imperial Graphic School in Vienna.

Secretary—Prof. Dr. F. Strohmer, Director of the Experiment Station for Beet-Sugar Industry, Vienna.

Respectfully,

H. W. WILEY, Dept. of Agriculture, Washington, D.C.,
Chairman.

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